IMPROVE
STANDARD OPERATING PROCEDURES

SOP 351
Data Processing and Validation

Date Last Modified	Modified by:
12/9/96	EAR
10/9/97	PHW

TABLE OF CONTENTS

Technical References

none

1.0 PURPOSE AND APPLICABILITY

This standard operating procedure (SOP) provides a general overview of the procedures for processing and validating IMPROVE data.

Data processing and data validation are performed in parallel. Most data validation checks are performed as part of the data processing procedures.

2.0 RESPONSIBILITIES

2.1 Project Manager

The project manager shall:

- oversee all aspects of the program
- review the seasonal quality assurance summary of the quality assurance specialist to determine if the data are acceptable for incorporation in the concentrations database

2.2 Quality Assurance Manager

The quality assurance manager shall:

- oversee all aspects of the program pertaining to quality assurance
- supervise the work of the quality assurance specialist
- review the seasonal quality assurance summary of the quality assurance specialist to determine if the data are acceptable for incorporation in the concentrations database

2.3 Quality Assurance Specialist

The quality assurance specialist shall:

- review the site configuration database for current flow rate calibrations
- review the site problems database for potential problems
- review the collection parameters in the database
- review the quality assurance summaries of the lab manager and the spectroscopist
- review the quality assurance summaries of the external contractors
- calculate concentrations and store in temporary database
- run appropriate level 2 data validation programs
- verify that there were no inconsistencies in analytical calibration
- examine individual inconsistent samples and determine the cause
- update the database with revised information (modify parameters or invalidate)
- recalculate concentrations
- rerun data validation programs
- present a quality assurance summary for each season with appropriate plots and tables to the quality assurance manager and project manager
- transfer the data to the final concentrations database

2.4 Field Specialist

The field specialist shall:

- maintain documentation on the flow rate calibration for each module
- verify that the flow rates are within acceptable tolerances

2.5 Laboratory Manager

The lab manager shall:

- oversee and maintain records on site and sampler operation
- review all log sheets for completeness, and to check the validity of the samples prior to downloading of the samples by lab technicians.
- resolve any inconsistencies on the log sheet or in the samples
- oversee entry of collection parameters in data base
- oversee entry of gravimetric analysis parameters in data base
- maintain documentation on daily gravimetric controls

2.5 Spectroscopist

The spectroscopist shall:

- maintain records on the operation and performance of the various analytical systems
- maintain documentation on standards and reanalysis for each analytical session
- oversee all technicians performing analyses and verify the correctness of the data entry

3.0 REQUIRED EQUIPMENT AND MATERIALS

none.

4.0 METHODS

This section deals with collection parameters of samples taken by the IMPROVE particulate sampler. These include the sampler and sample validation at levels 1 and 2.

4.1 Level 1 validation: Sampling validation

Four types of validation occur before filters and samples are accepted as valid.

Sampler equipment validation. (section 4.1.1)
Filter contamination validation (section 4.1.2)
Collection parameter validation (section 4.1.3)
Gravimetric and laser analysis validation (section 4.1.4)

4.1.1 Sampler equipment validation.

New samplers are tested at the Air Quality Group lab for leaks, wiring problems, and faulty parts. The sampler is completely assembled in the lab, then shipped to the site. Before the first samples are installed, an Air Quality Group technician verifies the correct installation, photographs and records details of the site, and leak checks and calibrates the sampler. This is done during installation or as the yearly maintenance (See SOP176, 201, 226).

4.1.2 Filter validation

Prior to acceptance for network use, all filter lots are tested for contamination. The Air Quality Group tests the Teflon and nylon filters; the contractors test the quartz and impregnated filters. The following is a summary of the acceptance procedures. For additional information, please refer to SOP 251.

Teflon (Gelman) filters are purchased by UC Davis in a single lot for an entire year.

a. Upon receipt from the Teflon filters vendor or manufacturer, one percent of the new filters are selected randomly throughout the lot for acceptance testing.
b. The selected filters are labeled and proceed through standard handling protocols.
c. Unexposed filters are analyzed by the XRF, PESA and PIXE systems for elemental artifacts.
d. Four A module IMPROVE samplers are set up side by side at the Evapotranspiration Field Test Site, and four sets of consecutive twenty-four hour samples are collected. The filters from these side by side tests are analyzed for artifact using PIXE, PESA, and XRF.

e. The Quality Assurance Manager interprets each test result and determines whether the new lot is acceptable. If no unusually large outliers are observed, the lot is certified as free of artifact.
f. When certified, the entire lot is accepted for use in Air Quality Group operations and payment to the vendor is authorized.

Gelman Nylasorb nylon filter material is purchased by UC Davis in 8.5" by 11" sheets from a single lot.

a. One 25 mm filter is punched from each sheet and the pressure drop for each filter is recorded to verify that the material is uniform throughout the lot.
b. Twenty filters are sent to the ion contractor to verify that there are no abnormal artifacts.
c. The Quality Assurance Manager interprets each test result and determines whether the new lot is acceptable. If no unusually large outliers are observed, the lot is certified for use.
d. Once accepted, filters are prepared from the sheets, four sheets at a time, and stored with spacers in standard 25 mm storage containers until required for use.
e. The remaining sheet stock is kept in a sealed container in a cool, dry, clean place until needed.

Quartz filters for fine carbon aerosols are purchased, pre-fired, and analyzed for artifact by an external contractor. Specific requirements and procedures are included in the IMPROVE SOP's Appendix 13. The pre-fired quartz filters are received and retained in a clean, cool, dry environment until required in the loading sequence.

Impregnated filters for measuring gaseous SO_2 as SO_4 are both supplied and analyzed for artifact by an external contractor. Specific requirements and procedures are included in the IMPROVE SOP Appendix 14. The impregnated filters are received and retained in a clean, cool, dry environment until required in the loading sequence.

4.1.3 Collection parameters

Once an exposed sample has been returned to the lab, the third phase of Level I validation occurs; filter validation prior to entry in the database.

Prior to downloading of the exposed filters from the cassettes, the field log sheet is checked for appropriate gauge readings, installation and removal date, sample duration, sample installation, and for operator errors. The cassette is checked for damage that could cause leaks, and the filter is inspected for holes, tears, or non-uniform deposit. A status code is assigned to all abnormal samples.

All normal samples are entered into the database, but only the abnormal samples assigned a status of questionable are entered. Abnormal samples are investigated and assigned a status of

either unusable or questionable. Unusable samples are archived without analysis and are stored separately.

Status codes indicating an unusable sample, one that is never entered into the database, are as follows:

NS: not serviced. The samples were either exposed for more than one sampling period, or for less than 75% of their normal sampling period. The operator did not service the site.

EP: equipment problem. A sampler malfunction made the samples invalid.

SE: site error. The filters were incorrectly installed by the operator.

PO: power outage. The sampler ran for less than 75% of a normal sampling period due to a power outage.

XX: invalid for other reasons. The sample ran for less than 18.00 hours, the filter has a hole, the filter has obvious problems (not centered properly, grill upside down), the filter was dropped or contaminated by water, the cassette is broken.

Samples that are questionable are processed normally, but the data is flagged and checked during the data validation procedures. The status codes and the accompanying reasons for including a sample in these categories are:

CG: clogged filter. The final magnehelic reading is less than 1/2 of the initial reading, resulting in unreliable flow rate measurements. (This sample is kept to document the factors involved in clogging,)

LB: laboratory blank. A quality assurance filter used to determine artifact levels due to laboratory procedures. It is not sent to the field, and it never samples air.

FB: field blank. A quality assurance filter used to determine artifact levels from the entire sampling process. It is handled as a normal filter, but it never samples air.

4.1.4 Gravimetric and laser analysis validation

Gravimetric analysis validation involves monitoring the precision and stability of the Cahn electrobalances. Twice per day, at 8:30 am and 1:30 p.m., the electrobalances are cleaned and calibrated. In the calibration procedure, the range is set, then the calibration standard weight is measured. If the standard weight is within two micrograms of it's average value and the calibration is stable, the electrobalance is considered calibrated. If either condition is not met, the balance is checked for malfunctions and repaired if necessary. The calibrations are

recorded in a log with data on the humidity, temperature, and magnetic field strength during calibration.
The zero value for the balance is checked after every five analyses. A change in the balance zero of one microgram or more during use may indicate a change in the calibration. When a change is observed, the balance is re-calibrated.

The hybrid integrating plate (HIP), laser analysis, validation involves monitoring the stability of the laser and detectors. Prior to the quarterly analysis, the laser and detectors are allowed to warm up for at least three hours. The laser is calibrated, and intensity in the forward and reflectance detectors is verified and recorded in the analysis log. The B93 Washington DC tray is analyzed in the laser system, and the values compared with previous analyses of that tray. If the correlation of the old and new analyses is good, the system is assumed to be operational. If the correlation is poor, the detectors, power supply, or alignment are checked and corrected.

During actual analysis, the laser intensity in the forward and reflectance detectors is monitored at the start and end of each analysis tray, and after every ten samples. If the intensity changes more than 1%, the laser is re-calibrated, and the previous ten samples are re-analyzed.

4.2 Level II Validation

Level II validation refers to quality assurance performed on measured or derived data in the Trayfile database. The five areas of verification are as follows:

flow rate consistency checks, (section 4.2.1)
quality assurance of gravimetric analyses (section 4.2.2)
quality assurance of laser analysis (section 4.2.3)
elemental analyses (section 4.2.4)
contractor analyses (section 4.2.5)

4.2.1 Flow rate consistency checks

Flow rate consistency checks are done upon entry of the field log sheet data, and at weekly, monthly and quarterly intervals for each site. If the initial flow rate is not within 5% of the nominal value, there may be a problem with the sample, or the sampler. These anomalous data are carefully checked to determine the cause and resolution of the problem, and corrective action is taken if necessary. If it becomes necessary, audits can be done through the mail (See SOP 176). The IMPROVE sampler is constructed with two independent gauges for flow measurements. If the primary gauge is determined to be malfunctioning, the database manager is notified to set the flow data pointer in the database to the secondary gauge.

Consistency plots of the flow history at a site provide a visual reference for sampler behavior, useful in resolving problems by displaying the chronic or sporadic behavior of the sampler flow (See Figure 1) . These consistency plots are generated on a weekly basis by maintenance personnel to find and correct problems, and a quarterly basis for quality assurance archives. The plots can be plotted on demand to include the most recent data. The plots can reveal flow inconsistencies due to logsheet errors, sampler malfunctions or other problems that must be resolved.

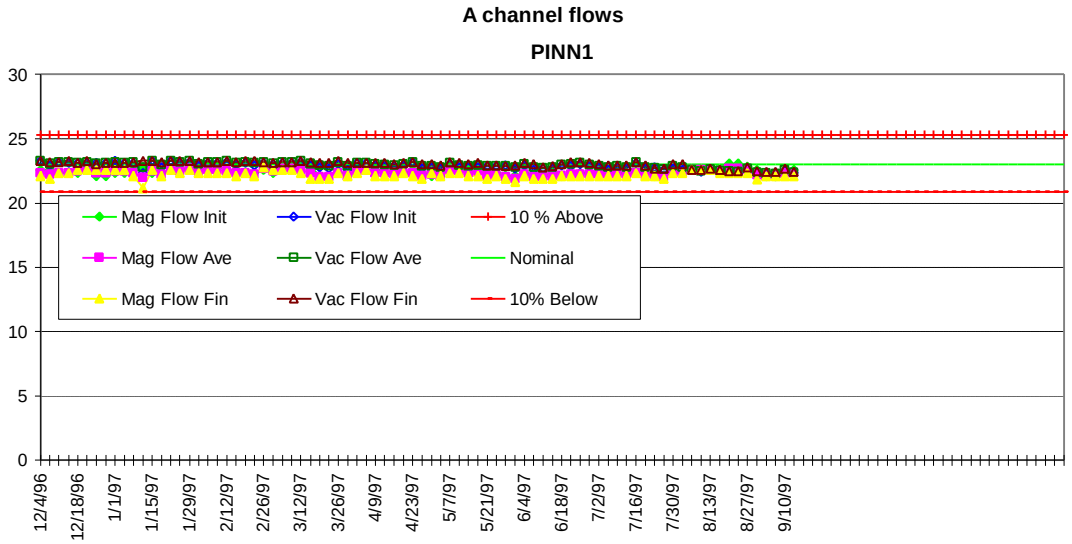

Figure 1. Sampler Flow monitoring

4.2.2 Quality assurance of gravimetric analyses

Gravimetric mass analysis is performed using Cahn 31 and Cahn 25 Electrobalances modified with a zero area bail and vertical counterweight. Polonium anti static strips are used to reduce electrostatic effects in the weighing cavity and on individual filters. Earth grounded conductive mats are used on the weighing table surface and technician foot surface to negate electrostatic effects. A segregated laboratory area controls human traffic and allows a stable temperature in the weighing environment. The area is cleaned daily with a high efficiency HEPA vacuum, and a tacky floor covering is installed to minimize dust artifact.

Gravimetric analysis of IMPROVE samples requires the collected or differential mass be determined through two weighings. Teflon filters are assigned a unique media identification, pre-weighed, post-weighed, analyzed and archived. The two weighing operations are identical and referred to as PRE and POST. Laboratory and field controls are utilized to determine mass artifact in the same manner, and to verify the correct operation of the electrobalance.

The initial quality assurance on gravimetric data is done upon entry of pre and post weights into the database. The technician weighing the filters checks the site, date, and media identification number and verifies the recorded mass. After post weighing, the differential mass (post weight minus pre weight) is derived by the computer, but must be accepted by the technician as a reasonable, non-negative number before it is recorded in the database.

Unusual differential masses are generally resolved before entering the database. If no resolution is found, the A module mass data is flagged, but is entered into the database. Later quality assurance procedures will deal with the problem. For D module filters, unresolved large negative masses are changed in status to XX and removed to the problem file, while unresolved large positive masses are flagged, but kept and entered into the database for further analysis.

The secondary quality assurance on gravimetric data occurs quarterly during construction of the PIXE instruction files. The differential masses are sorted by magnitude, and extremely large or negative masses are re-weighed for verification. Other possibilities such as sample mis-identification are considered, and the data are corrected if necessary. Also, the A channel gravimetric data, 2.5μm cut point, are compared to the D channel gravimetric data, 10μm cut point. If the A module gravimetric mass is the same size or larger than the corresponding D module mass, both are re-weighed and flagged if no resolution occurs. No data are removed from the database at this time. Filters with unresolved mass problems are analyzed normally.

The final Level II verification of mass data occurs after acquiring and processing the elemental data. Reconstructed mass values are generated from the elemental output from the elemental analysis, and these values are compared to the measured mass values. The measured and reconstructed mass should correlate well, with the reconstructed mass being between 85% and 100% of the measured mass. The percentage is site dependent and is generally reflected in historical data. If the percentage is substantially different from past values, or is out of range, there may be a problem with the weight measurement or the elemental analysis. The sampler flow, the sample duration, and the deposit area would be carefully verified, as well as the calibration values and re-analysis data from the PIXE run. The data manager and quality assurance manager would investigate and a resolution reached.

If all but one or two of the measured mass values at a site correlate well with the reconstructed mass values, the measured mass for these one or two points is considered suspect. If the A module gravimetric mass is larger than the D module gravimetric mass for the site and date in question, the A module gravimetric mass is assumed invalid and is flagged for deletion. If no clear decision can be made, the data manager is consulted and a resolution is reached.

4.2.3 Quality assurance of elemental analyses

Three analytical systems are used for elemental analysis of the Teflon filters. IMPROVE A module (2.5μm cut point) Teflon filters are analyzed in quarterly batches. All elemental analyses occurs during two quarterly analysis runs. The analyses and the quality assurance procedures associated with each can be found in the following sections:

X-Ray Fluorescence analysis, XRF, (section 3.2.3.1);
Proton Induced X-Ray Emission analysis, PIXE, and Proton Elastic Scattering Analysis, PESA (section 3.2.3.2);
Elemental data quality assurance (section 3.2.3.3);
Quality assurance of flow rate data (section 3.2.3.4)

Upon completion of these procedures, but before deleting invalid data, the data manager is consulted for approval. If approved, the data are deleted, and the deletions recorded in a log file for later reference. Only one deletion file for PIXE, PESA and XRF data is created for each quarter, and this is also saved for later reference. All of the quality assurance plots are reviewed by the data manager and archived for later reference.

4.2.3.1 X-Ray Fluorescence analyses

At the start of the analysis run, a tray of elemental standards is analyzed to provide data on the functioning of the XRF system, and to ensure the detector is working properly. The seventeen elemental standards purchased from Micro Matter Co. are the same type used for PIXE standards, and are analyzed in the PIXE system every twelve analysis runs to confirm the correlation between the XRF and PIXE systems shown by the re-analysis data. The elemental standards include single, double, and multiple element thin film standards and range in concentration from 20 to 60 micrograms per square centimeter. These standards are analyzed to ensure the detector is working properly, and to calibrate the acquisition system. The same standards are used for each quarterly analysis to provide continuity. Included in the standards tray are several unexposed filters, blanks, for determining the background spectra. The spectra of each blank is scrutinized for contaminants, and the cleanest blank is selected for use as the background subtract value. As a second check, this background subtract value is used on the re-analysis samples. If the spectra are not under or over subtracted, the blank is saved.

Once the standards have been deemed acceptable, two trays of samples analyzed during the previous run are re-analyzed. The data from this re-analysis is plotted against the data from the previous run. From the comparison of the standards, a re-normalization parameter, or RENO is determined. With the RENO applied to the re-analysis, the re-analyzed filters are compared to the data set taken during the previous run. This is a calibration value that removes the effect of variations in the x-ray beam between analysis runs. The re-analysis tray is run at the start and end of each ten day analysis period, roughly every thousand samples, or whenever the XRF system is shut off and turned back on. The analysis is done in ten day segments since the XRF system must be shut down and the detector refilled with liquid nitrogen on that time scale.

Once the XRF system has been turned off, it requires a three hour warm up period to allow the detector and the x-ray source to stabilize before it can be calibrated. Before continuing the analyses, the re-analysis tray must be analyzed and a new re-normalization parameter calculated. Generally, just before the XRF system is shut down, the re-analysis tray is analyzed to verify the current re-normalization factor.

Two system are used to collect and analyze the spectra from the detector. ACE collects the data from the detector and associates it with an analysis number. RACE processes the data from the detector into a file containing the sample identification, the quantity of each species found, the minimum detectable limits for each species (MDL), and the location and probable identification of peaks in the X-ray spectrum. It also does subtraction of the background value for the substrate. Users enter the run calibration values, and determine the optimal blank subtract. The output data is saved in files according to site and quarter or month, data for each sample given by the operator and the analysis instruction file.

Once the data have been collected, they are stored pending PIXE analysis of the samples. Further quality assurance analysis occurs in conjunction with PIXE data quality assurance, and will be discussed at that time.

4.2.3.2 Proton Induced X-Ray Emission and Proton Elastic Scattering Analysis

At the start and end of each analysis run, a tray of standards is analyzed. Thirty are elemental standards purchased from Micro Matter Co., six are Mylar blanks for PESA calibration, and two are unused (blank) Teflon filters. The elemental standards include single, double, and multiple element thin film standards and range in concentration from 20 to 60 micrograms per square centimeter. These standards are analyzed to ensure the detectors are working properly, to normalize the two PIXE detectors, and to calibrate the acquisition system. The same standards are used for each quarterly analysis to provide continuity. Every twelve analysis runs, the PIXE standards are analyzed in the XRF system and the PIXE system, and the results are compared to confirm the correlation between the two systems shown by the re-analysis data. The areal density the elements on the standards are measured and compared to the quoted values. The average of the ratio of the measured and quoted values is the re-normalization factor, RENO, for the analysis run, and negates differences between runs due to slight changes in the proton beam. If the RENO's are not between 0.9 and 1.1, with a standard deviation of less than 5%, the system is not considered adequate for sample analysis and the run is stopped until the problem can be rectified.

Once the standards have been deemed acceptable, a tray of samples analyzed during the previous run is re-analyzed. The data from the re-analysis is plotted against the data from the original analysis. From this comparison, an independent set of re-normalization factors, RENO's, is determined. The RENO's generated from the standards tray analysis and from the re-analysis tray should agree. If the values are not within 5%, the proton beam is checked for stability, and both trays are re-analyzed.

The re-analysis tray is analyzed every thousand samples, roughly three times during a standard analysis run, and whenever the proton beam is re-tuned. Generally, the same proton beam is used for an entire analysis run, so the re-analysis tray is run only three times. Re-normalization factors for the entire run are determined after the run is completed by doing best fit analysis after averaging all the collected RENO values.

The unexposed Teflon filters, blanks, in the standards tray are used to determine the PIXE background spectra. The spectra of each blank is scrutinized for contaminants, and the cleanest blank is selected for use as the background subtract value. As a second check, this background subtract value is tested on the re-analysis samples. The blank subtract should eliminate the background spectra that exist between elemental peaks, but should not eliminate any peaks.

Two system are used to collect and analyze the spectra from the detectors. ACE collects the data from each detector and associates it with an analysis number. RACE processes the data from each detector into separate files containing the sample identification, the quantity of each species found, the minimum detectable limits for each species (MDL), and the location and probable identification of peaks in the X-ray spectrum. It also does subtraction of the background value for the substrate. Users enter the run calibration values, and determine the optimal blank subtract. The output data is saved in files according to site and quarter or month, data given by the trayfile for each sample.

4.2.3.3 Elemental data quality assurance

Once the PIXE data have been collected, quality assurance procedures for the complete elemental analysis of the samples begins. This is usually done during the PIXE analysis run to reduce the chances of having a run that go beyond standard specifications. First, the XRF, then the PIXE and PESA data are re-examined to verify the calibration and blank subtract values used during the analysis runs. Parallel data sets are created, the XRF database having only XRF data, the PIXE database containing PIXE data , and PESA database containing the PESA data. A plotting program is used to compare the following species from each database for each sample: S, Ca, K, V, Ti, Mn, Fe, Ni, Cu, Zn, As, Pb, Se, Br, Sr, Rb, and Zr (See Figure 2). If the species do not correlate well, the data manager and PIXE manager are consulted. The calibrations and re-analysis data are checked, and a resolution is reached.

If the species all show good correlation, the following correlation plots are created:
gravimetric mass versus reconstructed mass,(MF vs. RCMA),

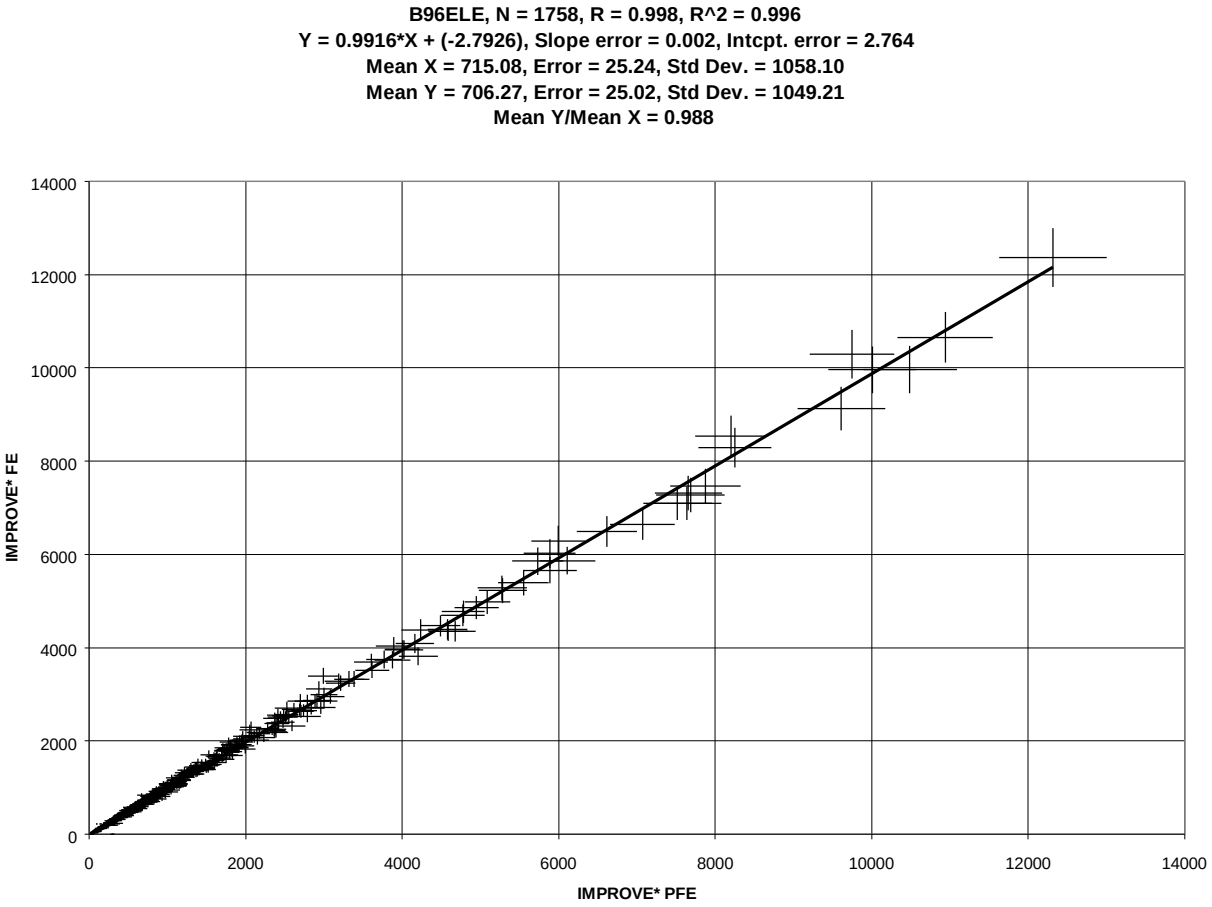

Figure 2. PIXE vs. XRF comparison

gravimetric mass versus hydrogen, (MF vs. H), and
silicon versus iron, (Si vs. Fe).
copper versus minimum detectable limit for copper (Cu vs. Mdl)
zinc versus minimum detectable limit for zinc (Zn vs. Mdl)
trace element concentration versus time

As these species should correlate well, poorly correlated data points are identified and scrutinized. If the stray points appear due to regional effects (i.e. seen at most of the sites in a region on or near that date), the data is considered valid. If the stray points do not appear to correlate to anything, it is possible that the data are incorrect.

A series of time plots of trace element concentration at each site are generated for the following species:
Se, Br, V, Pb, Ni, and As

These site specific plots show concentration versus time, and involve data from the current quarter as well as the previous four quarters (See Figure 3). If a step in the data is seen between quarters, the elemental analysis system is suspect, and the PIXE and XRF

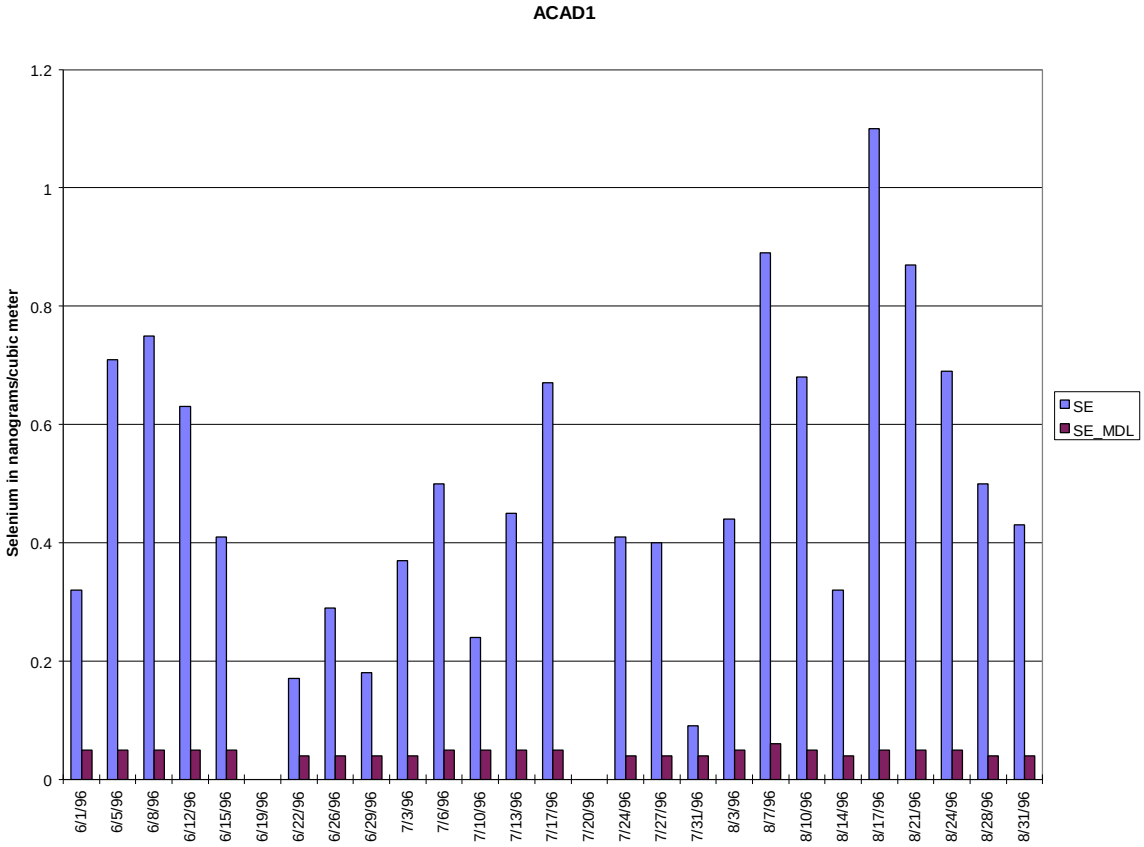

Figure 3. Time plot

calibrations and re-analyses are carefully reviewed by the data manager and quality assurance group until a resolution is reached. Slow trends in the data are due to regional effects.

Zinc versus the minimum detectable limit for zinc is plotted to verify that no zinc contamination was present on the filters. Zinc contamination, from the anodized sampler parts, would be in the form of large particles, if it existed. The percentage of zinc in a regional aerosol is generally constant, so outlier points having large zinc concentrations on the plot of Zn vs. Mdl would tend to indicate contamination (See Figure 4). An outlier is defined as being greater than three standard deviations from the correlation line. The data for each outlier point is flagged for review by the data manager.

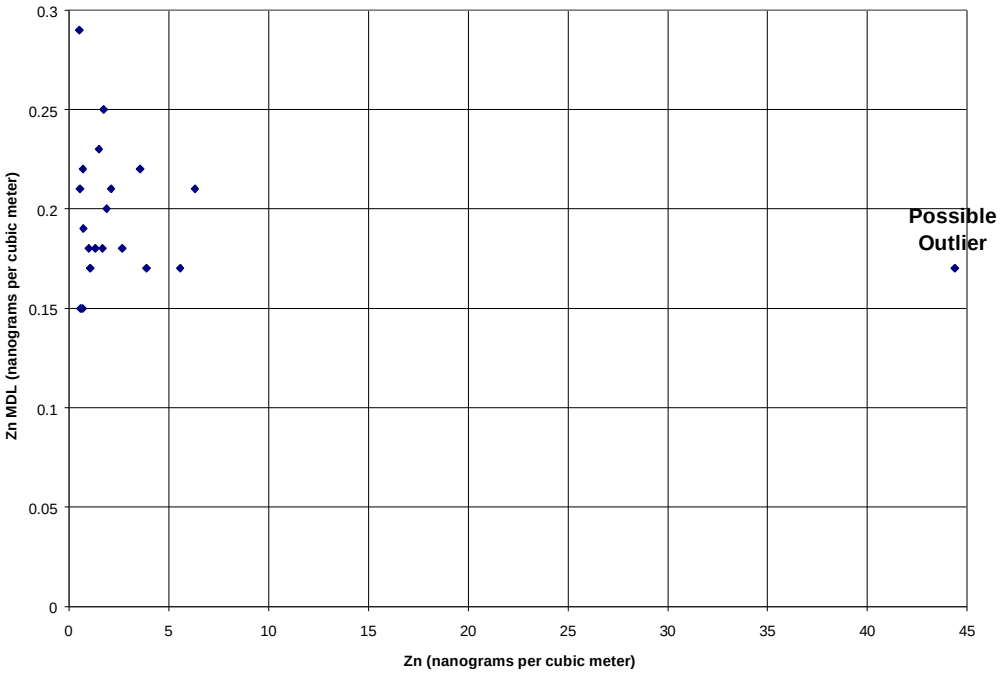

Figure 4. ZN vs. MDL for possible outliers

Copper versus the minimum detectable limit for copper is plotted, like zinc, to verify that no copper contamination from the brass fittings on the sampler is present on the filter. As in the Zn vs. Mdl plot, if outliers are found, they are flagged for review by the data manager.

The Si vs. Fe plots show site specific correlation, as both elements are primarily due to soils, and the ratios of these elements in the soils near a site are constant from year to year. Thus, this plot may be used as a secondary check of the XRF and PIXE calibrations, since Si is a PIXE element, while Fe is an XRF element. Poor correlation in the Si vs. Fe plot, unless historically common, would indicate a problem with the XRF or PIXE system calibrations and would result in review of these calibrations by the data manager.

The gravimetric mass versus H plot is meant to prove that PESA data was collected for all the samples. The plot also verifies the functioning of the PESA system since the ratio of organic matter to fine mass is roughly constant at four to five percent. Higher or lower ratios may indicate improper calibration of the PESA system, or invalid gravimetric mass data.

The gravimetric mass versus reconstructed mass plot is done as further quality assurance of the gravimetric data. Reconstructed mass, RCMA, is generated from data collected during analysis and does not include organic or nitrate contributions to the measured mass. RCMA generally correlates well with the fine gravimetric mass, MF, and stray data points are typically due to invalid gravimetric mass data. The measured and reconstructed mass should correlate well, with the reconstructed mass being between 85% and 100% of the measured mass. The percentage is site dependent and is generally reflected in historical data. If the percentage is substantially different from past values, or is out of range, there may be a problem with the sampler or the elemental analysis. The sampler flow, the sample duration, and the deposit area would be carefully verified, as well as the calibration values and re-analysis data from the PIXE run until the data were resolved. Invalid gravimetric data would be flagged for deletion.

4.2.3.4 Quality assurance of flow rate data

Quality assurance of the flow rate data for each sampler module are done upon receipt of the elemental, ion, carbon, and SO_2 data. One species is selected from each analysis procedure, and the concentration of the species is plotted against the uncertainty in the concentration (Figure 5). The uncertainty is a function of the volume of air samples, so if the flow rate is incorrect, the data will not fall on the correlation line. Outlier points are

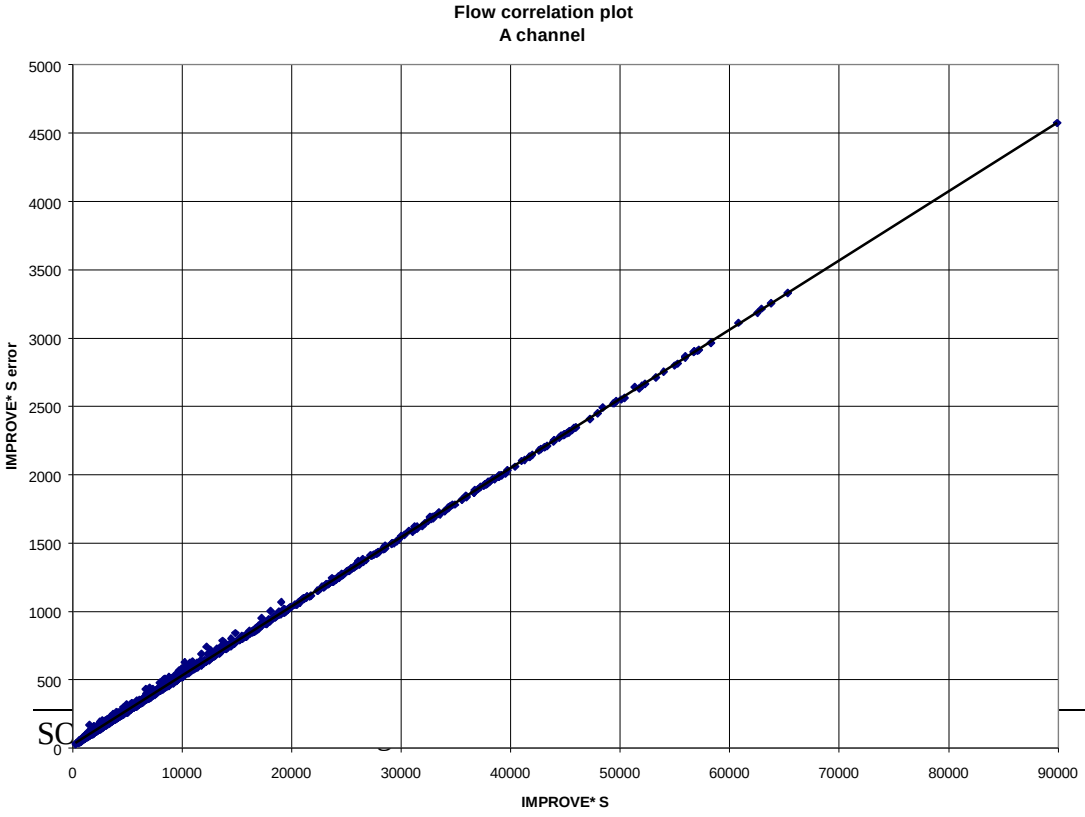

Figure 5. Flow rate quality assurance plot

data points that are located more than three standard deviations from the correlation line. For each outlier point, the flow rate and elapsed time are reviewed. If necessary, the data manager is consulted to reach a resolution. The species concentrations plotted against their uncertainties are as listed for each sampler module:

A module 2.5µm Teflon filter - Sulfur versus the uncertainty
B module 2.5µm Nylasorb filter - Sulfate versus the uncertainty
C module 2.5µm quartz filter - Light absorbing carbon (LAC) versus the uncertainty
D module 10µm Teflon filter - Total mass versus the uncertainty

4.2.4 Quality assurance of contractor analysis

Most Level II data validation for the Ion, Carbon and SO_2 analyses are done by the contractors responsible for the analyses. The contractor quality assurance procedures are recorded in Sections 12, 13 and 14 of the Appendix. The only Level II data validation for these samples done by the Air Quality Group is quality assurance of flow rate data, explained in Section 4.2.3.4.

4.3 Level III Validation

Level III validation refers to quality assurance performed through elemental or species comparisons between modules, and final review and approval of the data by the quality assurance group.

The B (Sulfates and Nitrates), C(Organic and Inorganic carbon), and D (PM_{10} , and, at some sites, SO_2) modules measures one or more species that are also measured by module A (H plus all elements from Na through Pb). This overlap allows verification of data through inter-comparison of samplers and analysis procedures. The following sampler module comparisons provide valuable information on the quality of the reported data:

A channel versus B channel data (section 4.3.1)
A channel versus C channel data (section 4.3.2)
A channel versus D channel data (section 4.3.3)
Regional data review (section 4.3.4)
Site summary review (section 4.3.5)
Final data review and validation (section 4.3.6)

4.3.1 A channel versus B channel data

Quality assurance for the A and B modules consists of comparison of the measured concentration of sulfur and sulfate (See Figure 6). Sulfur concentrations are reported through elemental analysis, while sulfate concentrations are derived through ion chromatography analysis. Since both modules sample simultaneously and have the same flow and aerosol size cut point, the collected data should correlate.

Any data more than three standard deviations from the correlation line are considered to be outlier points. All outlier points are carefully reviewed for flow rate entry errors, or analytical errors. Corrections are made and unresolved outlier data are flagged for review by the data manager and quality assurance group.

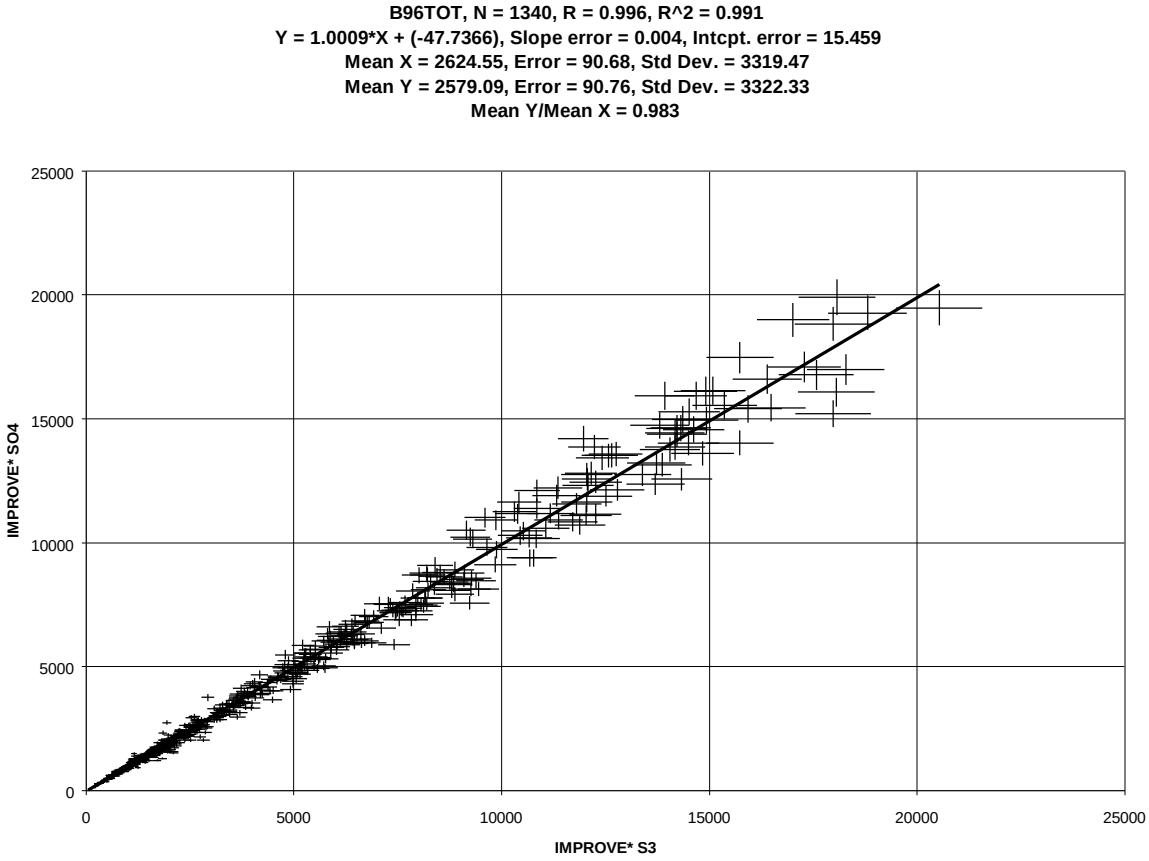

Figure 6. Elemental Sulfur vs. Ionic Sulfate

4.3.2 A channel versus C channel data

Quality assurance for the A and C modules involves correlation plots of four species, two from each analytical technique.

The first correlation plot is of B_{abs} and the measured concentration of light absorbing carbon (LAC). (See Figure 7) B_{abs} values are determined through hybrid integrating plate system (HIPS) analysis, while LAC concentrations are derived through thermal optical reflectance (TOR) analysis. Since both B_{abs} and LAC are measurements of light absorbing carbon, and both modules sample simultaneously and have the same flow and aerosol size cut point, the two measurements should within reason.

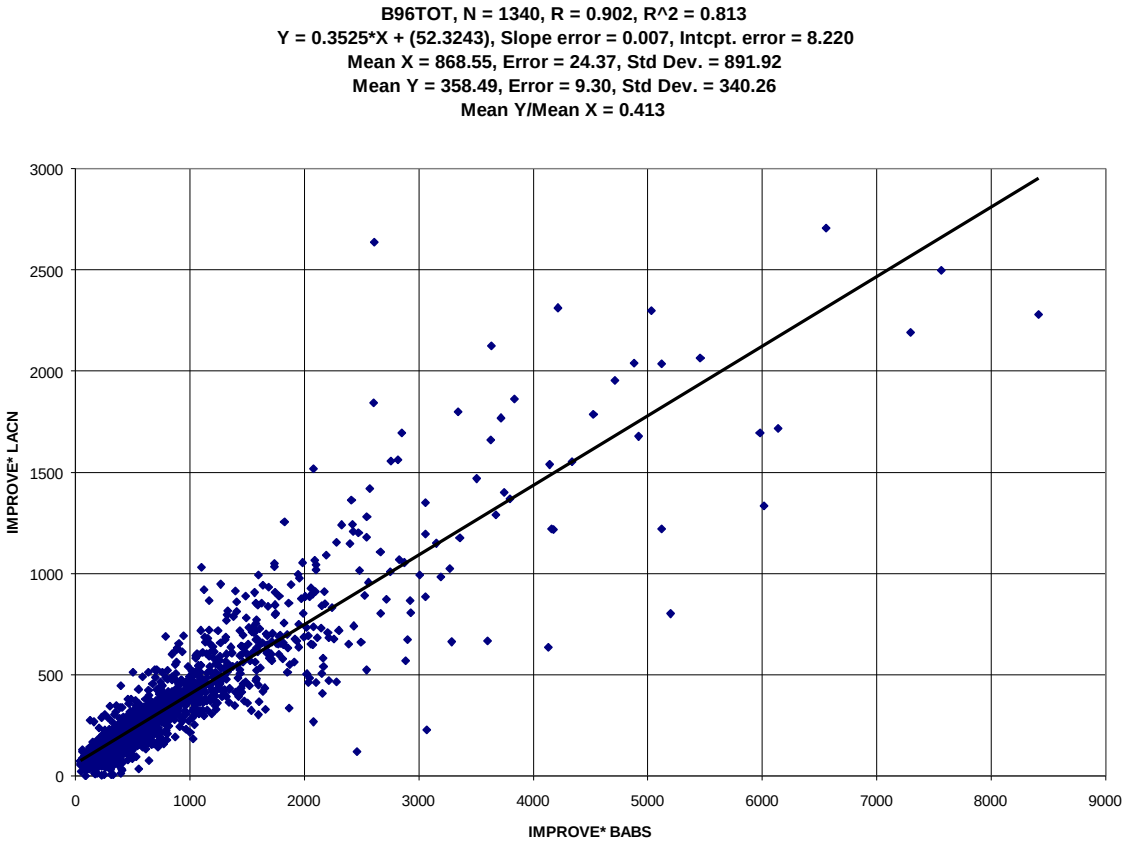

Figure 7. B_{abs} vs. LAC

The second correlation plot is of the concentration of organic mass from hydrogen analysis (OMH) and the concentration of organic mass from carbon analysis (OMCN). See Figure 8. OMH concentrations are determined by assuming that all sulfur is in the form or ammonium sulfate, no hydrogen is associated with nitrates, and the remaining hydrogen measured by PESA is from organic compounds. OMC concentrations are derived through thermal optical reflectance (TOR) analysis. Although OMH is merely an approximation of organic carbon, since both modules sample simultaneously and have the same flow and aerosol size cut point, the two measurements correlate well.

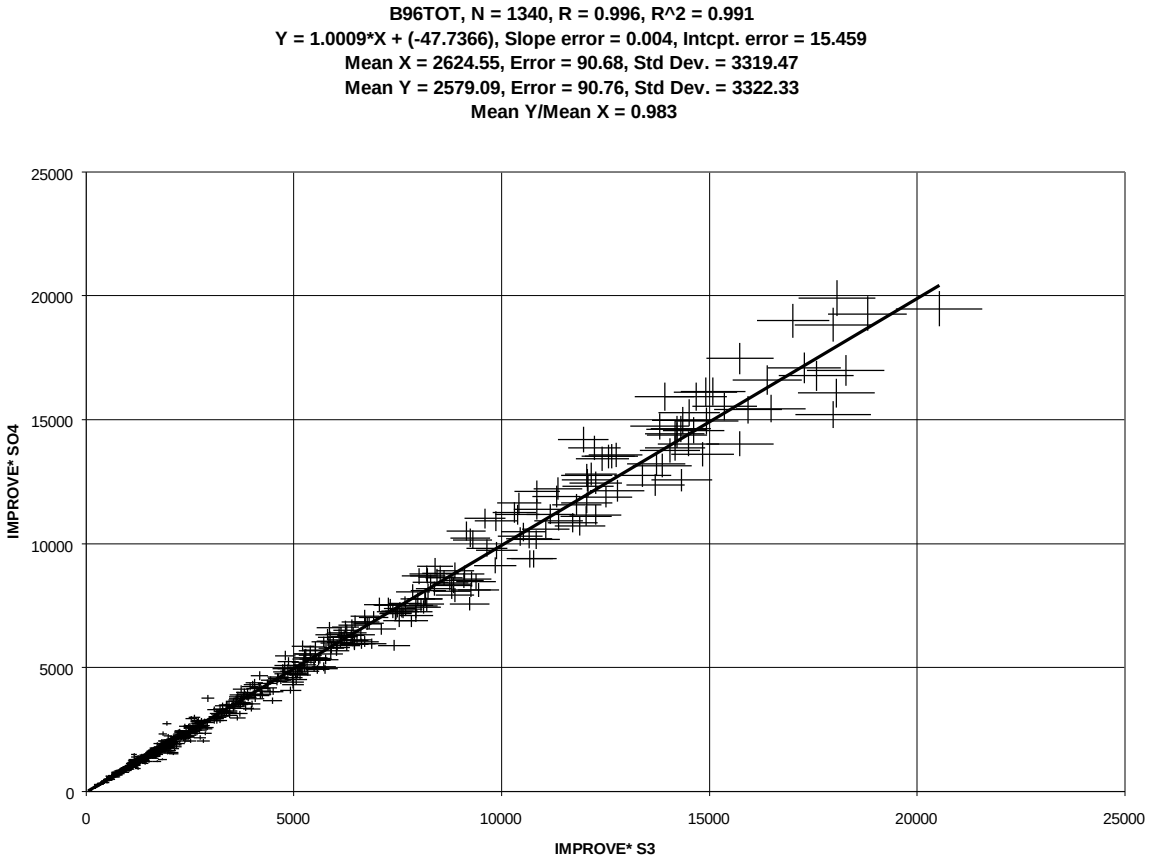

Figure 6. Elemental Sulfur vs. Ionic Sulfate

4.3.2 A channel versus C channel data

Quality assurance for the A and C modules involves correlation plots of four species, two from each analytical technique.

The first correlation plot is of B_{abs} and the measured concentration of light absorbing carbon (LAC). (See Figure 7) B_{abs} values are determined through hybrid integrating plate system (HIPS) analysis, while LAC concentrations are derived through thermal optical reflectance (TOR) analysis. Since both B_{abs} and LAC are measurements of light absorbing carbon, and both modules sample simultaneously and have the same flow and aerosol size cut point, the two measurements should within reason.

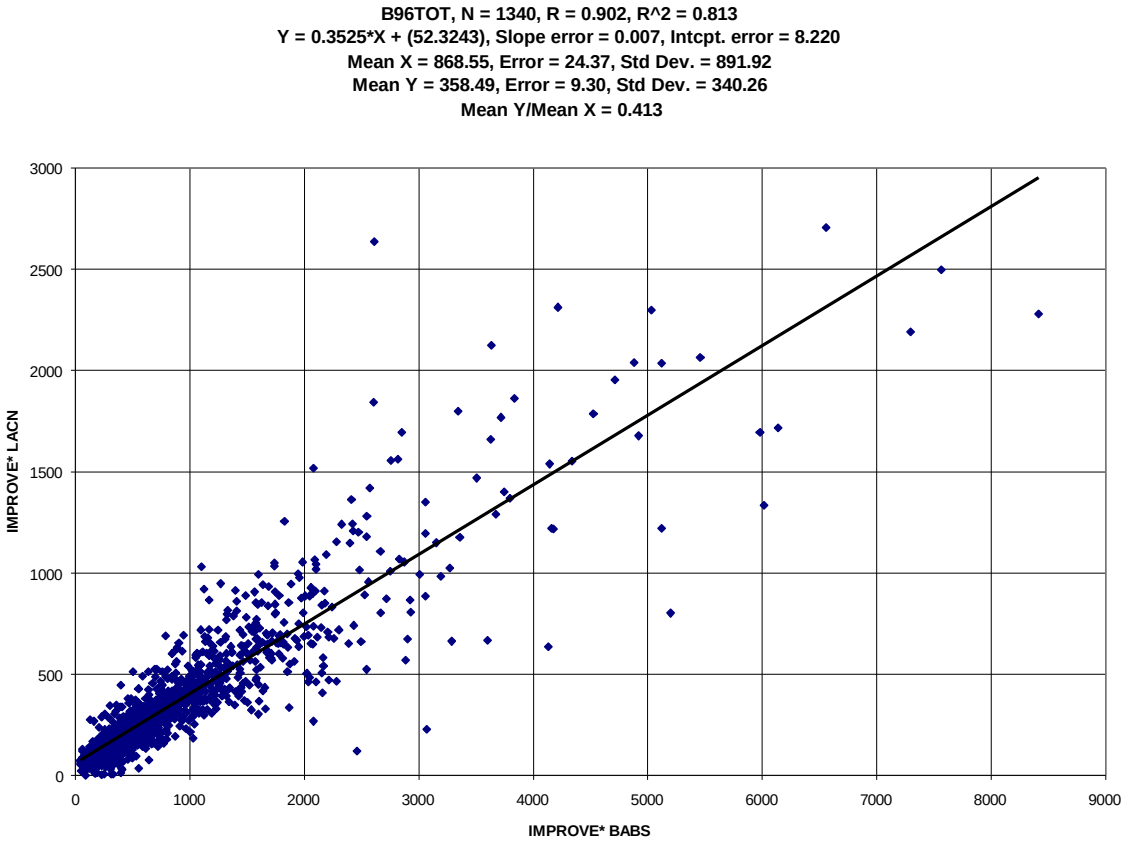

Figure 7. B_{abs} vs. LAC

The second correlation plot is of the concentration of organic mass from hydrogen analysis (OMH) and the concentration of organic mass from carbon analysis (OMCN). See Figure 8. OMH concentrations are determined by assuming that all sulfur is in the form or ammonium sulfate, no hydrogen is associated with nitrates, and the remaining hydrogen measured by PESA is from organic compounds. OMC concentrations are derived through thermal optical reflectance (TOR) analysis. Although OMH is merely an approximation of organic carbon, since both modules sample simultaneously and have the same flow and aerosol size cut point, the two measurements correlate well.

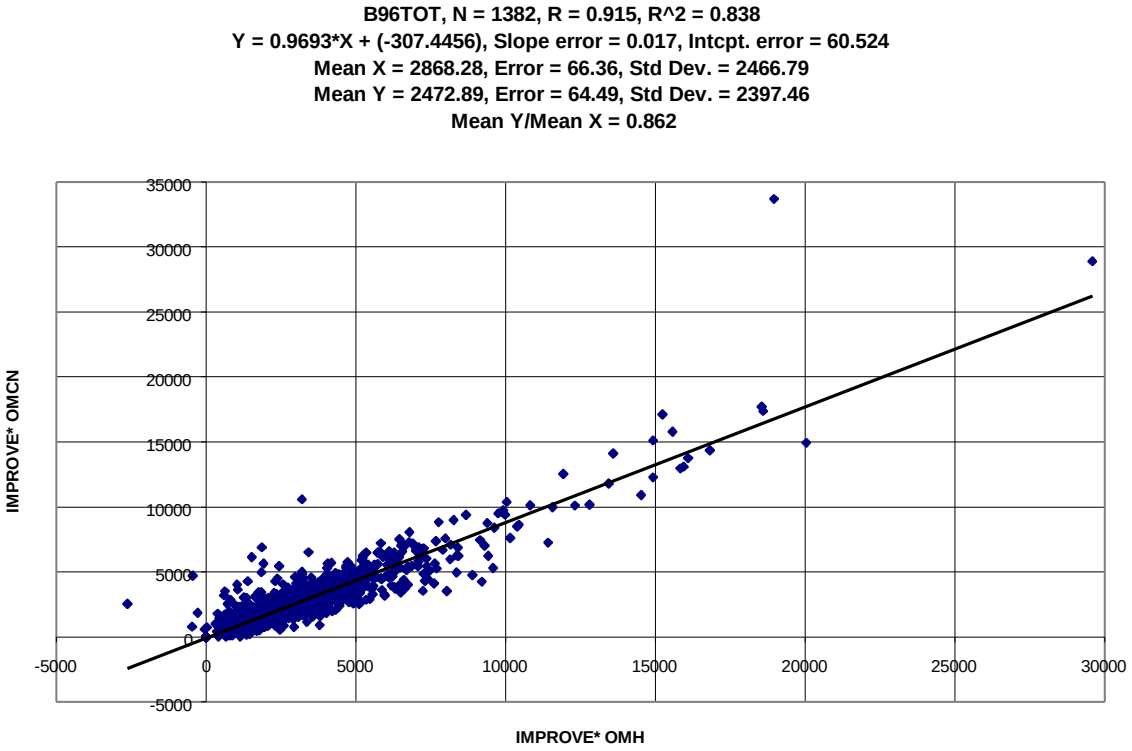

Figure 8. OMH vs. OMC.

For quality assurance, any data more than three standard deviations from the correlation line are considered to be outlier points. All outlier points are carefully reviewed for flow rate entry errors, or analytical errors. Corrections are made and unresolved outlier data are flagged for review by the data manager and quality assurance group.

4.3.3 A channel versus D channel data

Quality assurance for the A and D modules consists of comparison of the $PM_{2.5}$ mass concentration and the PM_{10} mass concentration. (See Figure 9) This procedure is done to verify that no $PM_{2.5}$ mass values are larger by two standard deviation than the corresponding PM_{10} mass values, and as another check of the sampler flow rates.. Although the ratio of $PM_{2.5}$ mass to PM_{10} mass is fairly consistent at most sites, the correlation plot is meant only to verify that no $PM_{2.5}$ mass values are larger than the corresponding PM_{10} mass values.

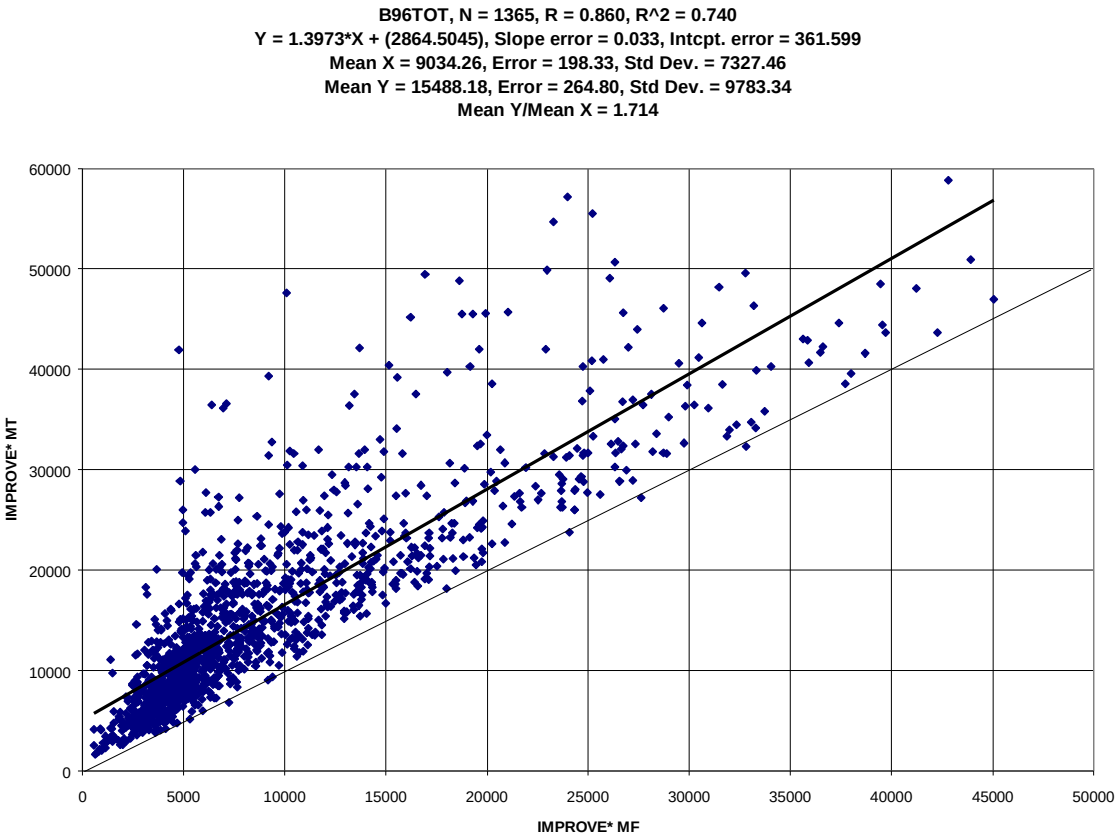

Figure 9. MF vs. MT

4.3.4 Regional data review

Most sites in the IMPROVE network fall into one of two groups, according the sampling conditions and the historical data.

The Eastern sites are those which historically have high humidity in the summer, are East of the Mississippi River, have relatively larger mass loadings, and proportionally higher sulfur concentrations.

The Western sites are those which historically have low humidity, are west of the Mississippi River, have relatively lower mass loadings, and proportionally higher soil concentrations.

Sites not included in this group are included in the All Sites group, though this grouping is less effective for quality assurance than the Eastern or Western groups.

For each group, Eastern, Western, and All Sites, the following correlation plots are created:
gravimetric mass versus reconstructed mass,(MF vs. RCMA - See Figure 10),

gravimetric mass versus hydrogen, (MF vs. H), and
sulfate versus sulfur, (BSO4 vs. S)
organic mass from carbon versus organic mass from hydrogen (OMC vs. OMH)

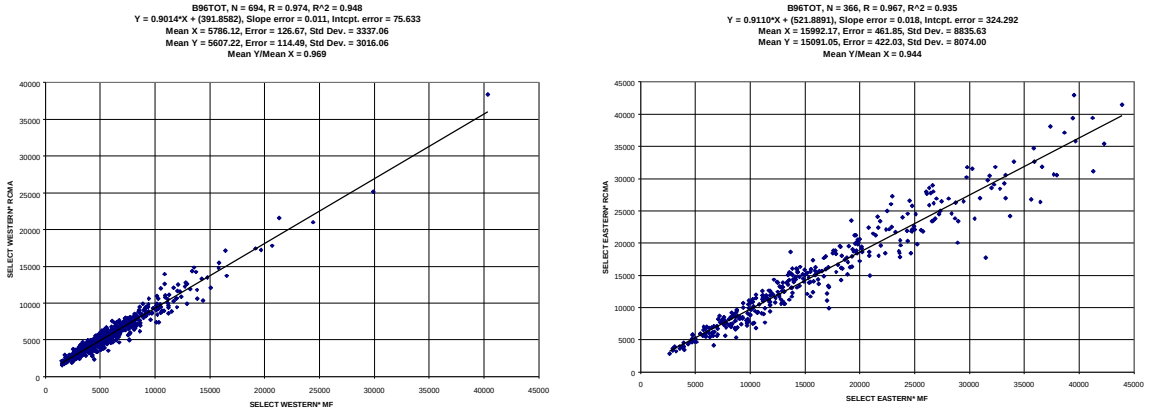

Figure 10. Select West and East plots.

Reviewing these data as part of a group having similar characteristics enhances recognition of differences. Since these sites are historically similar, differences noted in the current data may be due to sampler calibration problems, or to changes in the aerosol sources or removal mechanisms near the site. These possibilities are investigated, and the problem resolved and recorded. Since the IMPROVE network is concerned with regional aerosols, the addition of local sources must be noted and reported with the final data set.

4.3.5 Site summary review

The data for each site are recorded on quarterly summary output sheets.
Recorded species concentrations are compared to their associated minimum detectable limits (Mdl's) to verify the validity of the data. The Mdl's are compared with historical site Mdl's to insure they are reasonable. Samples having unusually large Mdl's are reviewed for sampler calibration or elemental analysis problems. (See Figure 11)

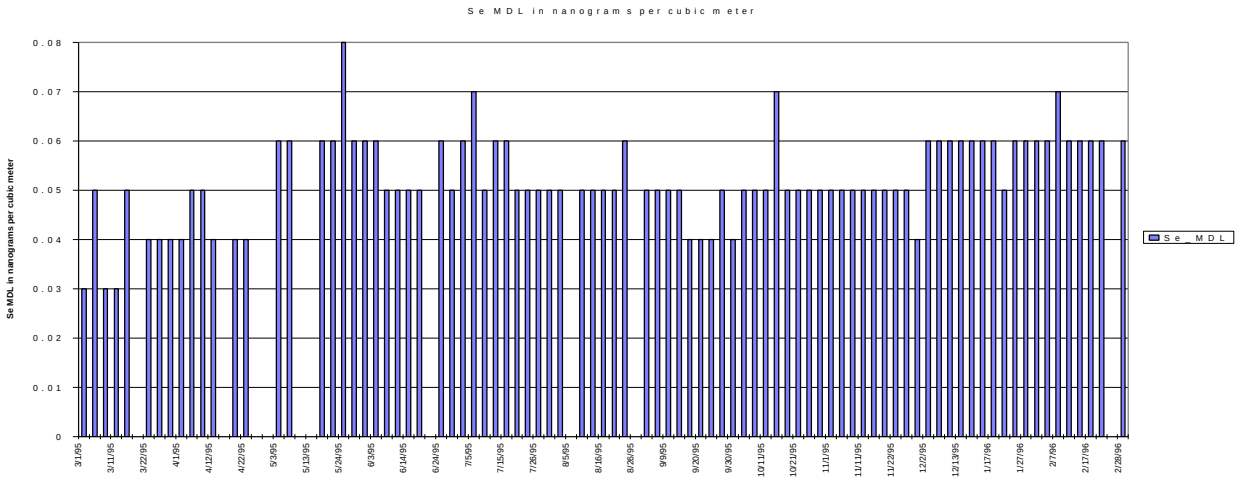

Figure 11. MDL plot

Finally, all missing data is noted and flagged for verification of invalid status.

4.3.6 Final data review and validation

Once all data corrections have been entered, and the data have been processed to their final form, the archived information for the quarter is submitted to the quality assurance group. Any remaining problems are resolved, and the final data set is agreed upon.

4.4 Modification and Documentation of Parameters

All parameters in any database that are changed are logged into the computer. The parameters can be changed only by restricted programs. Access to these programs are limited to key personnel, including the QA manager. The main program that has the ability to modify the IMPROVE databases is called Auxdata. Auxdata is a versatile program that allows the QA manager/specialists to view and/or edit the aerosol databases. The main screen displays the status of each of the samples and gives a menu of functions such as editing and background analysis. (See Figure 10) This interface allows access to all the databases referred in SOP 251. Following the procedures outlined earlier in this document, the user may have the need to modify the databases. Auxdata is the only program that will allow changes to databases.

In addition to edits, the program creates several files for additional quality assurance and for use by end users here at UCD. These files can be used by other programs created by the end user for reports or other statistical analysis.

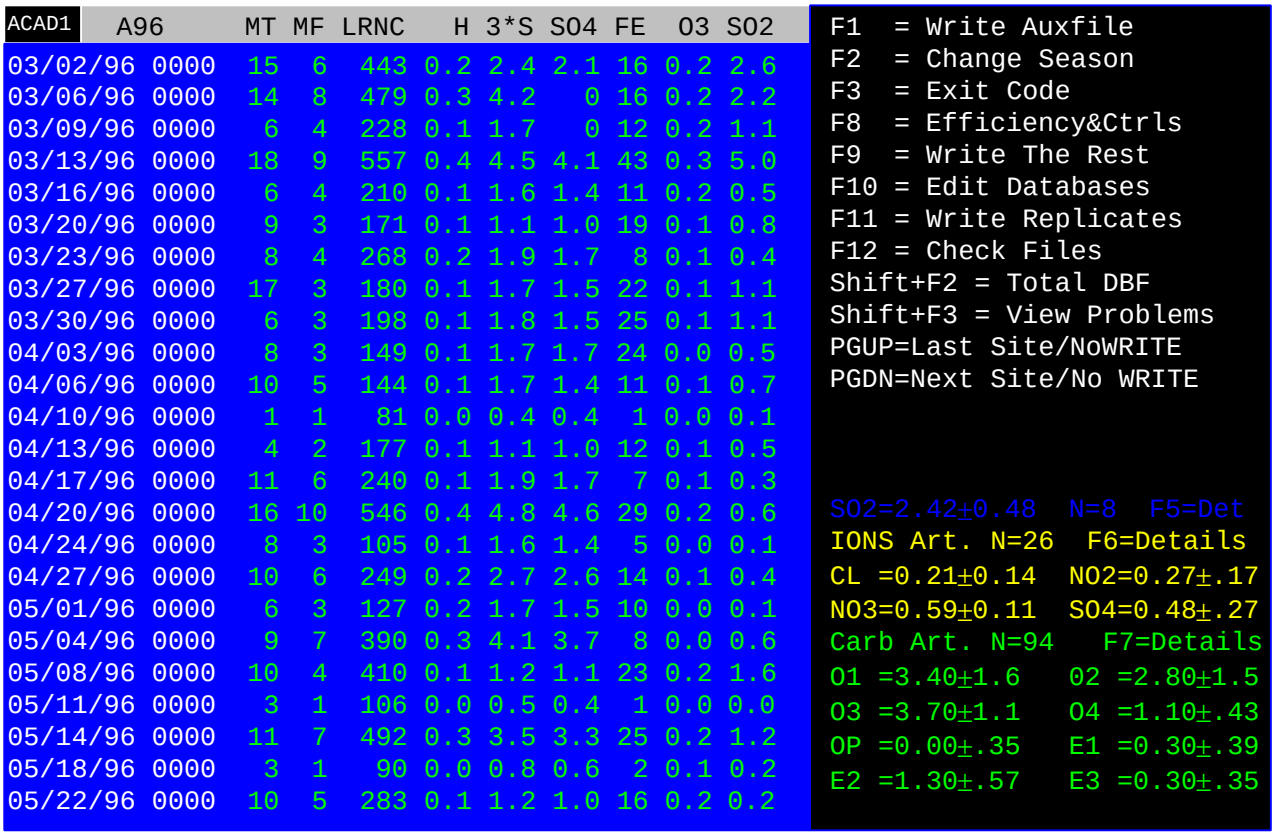

Figure 10. Auxdata Main Screen

4.4.1 Main screen displays

The main screen of Auxdata provides the user with an interface to view and/or edit the database. The screen also provides data relevant to quality assurance. The main screen is divided into three sections:

Data Summary;
Control Options;
Artifact Summary

4.4.1.1 Data Summary

The data summary section contains a quarterly summary of a particular site and quarter that the user wants to view. The user can choose the site by entering the site code in the designated box (e.g. ACAD in figure 10). The quarter can be entered by entering the "TAB" key and typing the 3 symbol quarter designation (e.g. A96 in figure 10). Once entered, the display is updated with the current data set. The screen will display the current status of each modules' data.

The list of species displayed presents an overview the samples status. MT shows the status of the D module. The MF shows the status of the gravimetric analysis of the A module. LRNC shows the status of the laser analysis. H shows the status of the PESA analysis. 3*S shows the status of the PIXE analysis. SO4 shows the status of the Ion analysis. Fe shows the status of the XRF analysis. O3 shows the status of the Organic analysis. SO2 shows the status of the SO_2 analysis. The status codes displayed are identical to the ones described in section 4.1.3. In addition to theses statuses, the following statuses may be displayed:

NI - Sample analysis not completed or in house
SO - Samples still out in the field
NA - Samples for this species is not available or not applicable

4.4.1.2 Control Options

The control option portion of the screen lists the options available by "hot key". The options are as follows:

F1 = Write Auxfile
Creates an ASCII file of contractor data for quality assurance
F2 = Change Season
Changes season
F3 = View Comments
View the comments from the logsheets
F4 = Exit Code

Exit code
F8 = Efficiency&Ctrls
Shows a table of the number of samples collected and laboratory controls.
F9 = Write The Rest
Writes the rest of the Auxfiles starting with the site outputted on the screen and working down alphabetically
F10 = Edit Databases
Allows user to edit the databases
F11 = Write Replicates
Produces a summary of all samples that are reanalyzed and compares to the original
F12 = Check Files
Check files for duplications, deletes and other abnormalities
Shift+F2 = Total DBF
Creates a single database for quality assurance tests
Shift+F3 = View Problems
Views a problem file that records any past problems from that particular site
PGUP=Last Site/NoWRITE
Moves up to the next site
PGDN=Next Site/NoWRITE
Moves down to the next site.

4.4.1.3 Artifact Summary

The portion of the screen displays the artifact or blank subtraction from the various contractors. They included SO_2, ions and carbon analysis. The numbers are based on field blanks taken during the quarter of analysis.

4.4.2 Subscreens

This option is still under construction and is meant to enhance the viewing of the IMPROVE database. This may included other graphical or textual representation of the data set.

4.5 Calculations

This section deals with the equations used to determine the various derived parameters. They are given in the following sections:

Flow Equations (4.5.1);
Determination of Concentration, Artifact, and Precision (4.5.2);
Equations of Composite Variable (4.5.3).

4.5.1 Flow Equations

The following section derives equations used to determine the flow rate and other aspects of aerosol sampling. This section is divided in the following manner:

The Effect of Flow Rate on Cyclone Cut Point (4.5.1.1);
Flow Control by a Critical Orifice (4.5.1.2);
Flow Rate through an Orifice Meter (4.5.1.3);
Pressure-Elevation Relationships (4.5.1.4);
Calibration of Audit Devices (4.5.1.5);
Nominal Flow Rate Equation (4.5.1.6);
Flow Rate Equations for the System Vacuum Gauge (4.5.1.7);
Calibration of the System Orifice Meter and Vacuum Gauge (4.5.1.8)

4.5.1.1 The Effect of Flow Rate on Cyclone Cut Point

The collection efficiency of the IMPROVE cyclone was characterized at the Health Sciences Instrumentation Facility at the University of California at Davis. The efficiency was measured as a function of particle size and flow rate using two separate methods: PSL and SPART. Both use microspheres of fluorescent polystyrene latex particles (PSL) produced by a Lovelace nebulizer and a vibrating stream generator. The PSL method analyzed these by electron micrographs, while the SPART method analyzed them by a Single Particle Aerodynamic Relaxation Time analyzer. The aerodynamic diameter for 50% collection, d_{50}, was determined for each flow rate. The relationship between diameter and flow rate is shown in Figure 11.

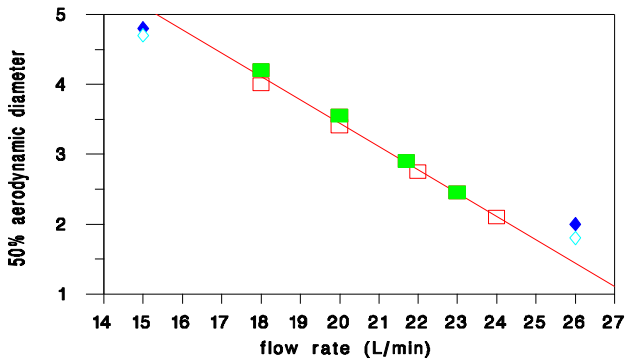

Figure 11: Relationship between 50% aerodynamic diameter and flow rate for the IMPROVE cyclone. The solid symbols are from PSL and the open symbols from SPART.

The best-fitting straight line in Figure 11 is based on measurements for both methods for flow rates between 18 and 24 L/min. The equation is:

$$d_{50} = 2.5 - 0.334 * (Q - 22.8) \quad \text{.....(351-1)}$$

with a correlation coefficient of $r^2 = 0.991$. In order to maintain a constant cutpoint of 2.5 µm, it is necessary to maintain a constant volume flow rate of 22.8 L/min.

4.5.1.2 Flow Control by a Critical Orifice

The flow rate through each module of the IMPROVE sampler is maintained by a critical orifice, located between the filter and pump. The device in the sampler is a removable brass plug with a small orifice. We have a range of available orifice diameters; in addition, the orifice can be slightly enlarged or decreased in the field. As long as the pressure after the orifice is than 52% of the pressure in front of the orifice, the air flow will be critical, that is, limited by the speed of sound and will not be affected by small changes in pump performance.

The mass flow rate is constant at all points in the system, but the volume flow rate increases as the pressure of the air decreases when the air passes through different stages. The concentration depends on the volume of ambient air, so we are concerned with the volume flow rate through the inlet. Since there is negligible pressure drop across the inlet, this is equal to the volume flow rate at the cyclone. This volume flow rate at the cyclone determines the cutpoint of the cyclone. The pressure will decrease as the air passes through the filter. If the pressure drop is ΔP, then the inlet flow rate is (1- ΔP) times the flow rate at the front of the critical orifice.

The flow rate through a critical orifice depends on the geometry of the orifice (primarily the diameter) and the absolute temperature of the air at the front of the orifice. We will assume

that this temperature is the same as the ambient temperature. The flow rate at the critical orifice differs from the inlet flow rate because of the pressure drop as the air passes through the filter. We have chosen to express all calibrations relative to a common temperature, 20°C. The equation for the inlet flow rate is

$$Q = Q_O * \left(1 - \frac{\Delta P}{P}\right) * \sqrt{\frac{T + 273}{293}}\ , \qquad (351\text{-}2)$$

where Q_O is a constant and $\Delta P/P$ is the relative decrease in pressure before the orifice. The pressure drop ΔP is produced primarily by the filter, either because of the pressure drop of a clean filter or because of filter loading. To account for the pressure drop of the clean filter, each critical orifice is adjusted during calibration to give the desired flow rate with a typical clean filter appropriate for the module. The important pressure quantity is the variation, δP, about the nominal pressure drop of the clean filter used in calibration, ΔP_{nom}:

$$\delta P = \Delta P_{nom} - \Delta P \qquad (351\text{-}3)$$

If δP is associated with variation in the clean filter, it can be either negative or positive, and will affect the measurements before and after collection equally. If the variation is caused by filter loading; δP will be positive and affect only the final flow rate measurement. For this reason we average the two readings.

The annual mean temperatures for all the IMPROVE sites, based on the weekly temperature measurements is 15°C. In order to have the mean annual flow rate at 22.8 L/min, the critical orifices are adjusted to provide a flow rate of 23 L/min at 20°C with a typical filter in the cassette. The constant Q_O in Equation 351-2 is then given by

$$Q_O = 23.0 * \left(1 - \frac{\Delta P_{nom}}{P}\right)^{-1}\ , \qquad (351\text{-}4)$$

The nominal flow rate is set at 19.1 L/min at 20°C for the Wedding PM_{10} inlet, and at 17.8 L/min for the Sierra-Anderson PM_{10} inlet.

Substituting Equation 351-4 into Equation 351-2, and assuming there is no variation in atmospheric pressure at the site, the flow rate is given by

$$Q = 23.0 * \left(1 - \frac{\delta P}{P - \Delta P_{nom}}\right) * \sqrt{\frac{T + 273}{293}}\ , \qquad (351\text{-}5)$$

Effect of Temperature and Pressure Drop on Cyclone Efficiency

Variations in temperature with site and season affect the collection cut point but not the volume calculation. The mean annual d_{50} will be slightly lower at warm sites than at cold. Saguaro (22°C) would have an annual d_{50} of 2.4 µm, while Denali (2°C) would have a d_{50} of 2.7 µm. For a given site, the mean d_{50} in summer will be lower than in winter. For example, based on historical records, the d_{50} at Davis would vary between 2.4 µm in midsummer and 2.6 µm in midwinter. At the highest maximum temperature recorded at Davis (34°C), the d_{50} would drop to 2.2 µm.

The Table 351-1 gives the variation in flow rate Q and d_{50} as a function of temperature, using Equations 351-5 and 3511-1, with δP zero.

Table 351-1. Flow rate and 50% aerodynamic diameter *vs.* flow rate.

T (°C)	-20	-10	0	10	20	30	40	50
Q (L/min)	21.4	21.8	22.2	22.6	23.0	23.4	23.8	24.1
d_{50} (µm)	3.0	2.9	2.7	2.6	2.4	2.3	2.2	2.1

Because the flow rate is measured before and after each sample, variations in ΔP also affect the collection cut point more than the volume calculation. The decrease in flow rate because of filter loading is accounted for in the volume calculation by averaging the values before and after collection. In general, filter loading is not a problem. For a typical western site, Canyonlands, the mean final flow rate over a recent 12-month period was 1% lower than the mean initial value. (The precision for reading the gauges is approximately 2%.) For a heavily loaded eastern site, Shenandoah, the difference of means was 3%. In the worst case, the flow rate dropped 15%; this increased the cut point from 2.3 µm to 3.5 µm.

The mean measured flow rates for the 49 sites of the IMPROVE network for the annual period from June 1991 to May 1992 indicate that in practice the combination of temperature and δP produce only a small variation in flow rate. The standard deviation at each site ranged from 0.2 L/min to 1.2 L/min, corresponding to standard deviations in d_{50} of 0.1 to 0.4 µm. In addition, the flow rate for all samples was close to the target value of 22.8 L/min. The mean flow rate was 22.5 ± 0.6 L/min, corresponding to d_{50} of 2.6 ± 0.2 µm.

Effect of Temperature and Pressure Drop on the Volume Calculation

The major error in volume calculation would occur when the mean temperature for a 24-hour sample differs significantly from the mean temperature of the two readings during the sample changes. Normally this is not a significant problem, but could occasionally occur. A difference of 5°C would produce an error of 1%, while a 10°C difference would produce an error of 2%.

4.5.1.3 Flow Rate through an Orifice Meter

An orifice meter consists of a restriction in the air path and a device to measure the pressure drop across the restriction. Three orifice meters are used in the IMPROVE network, all using magnehelics to measure the pressure drop. The audit devices consists of an assembly that fits into the base of the inlet tee of the fine modules and at the base of the inlet stack or the PM10 module. For the fine modules, the assembly stops the normal flow through the inlet. For all modules, the air flow must pass through a calibrated orifice in the assembly. The audit devices are calibrated at Davis using a spirometer. The fine modules use a system orifice meter based on the restriction produced by the cyclone. The PM10 module uses an orifice meter located between the filters and the pump.

The flow rate through an orifice meter depends on the pressure drop across the restriction and the square root of the density of the air:

$$Q = Q_1 (\delta P)^{\beta} \sqrt{\frac{P_o}{P}} \sqrt{\frac{T+273}{293}} \quad \text{.....(351-6)}$$

where Q_1, β, and P_O are constants. For laminar flow, $\beta = 0.5$. We express Equation 351-6 in parameterized form using the magnehelic reading, M, for the pressure drop:

$$Q = 10^{a} M^{b} \sqrt{\frac{P(\text{sea level})}{P(\text{site})}} \sqrt{\frac{T+273}{293}} \quad \text{.....(351-7a)}$$

We have arbitrarily defined all pressures relative to the standard pressure at sea level and all temperatures relative to 20°C. Thus, the parameters, a and b, are always calculated relative to 20°C and Davis. The value of b should be similar to that of β, around 0.5. The advantage in expressing the parameters relative to sea level is that all modules should have parameters with similar values independent of the site elevation.

Because of the difficulties in measuring the ambient pressure at each sample change, we have chosen to use an average pressure based on the elevation of the site. The pressure-elevation

function is discussed in Section 4.5.1.4. We will write the pressure and temperature functions as F(elev) and f(T):

$$F(elev) = \sqrt{\frac{P(sea\ level)}{P(site)}} \qquad f(T) = \sqrt{\frac{T + 273}{293}} \ .$$

Thus, Equation 351-7a can be written

$$Q = 10^{a} M^{b} F(elev)\ f(T) \quad \text{..... (351-7b)}$$

Because the PM10 orifice meter is located after the filter, where the air density is lower than the inlet density, the inlet flow rate does not follow Equation 351-6. Using the equation for an orifice meter and Equation 351-2, the equation for the inlet flow rate is

$$Q = Q_2\ (\delta P)^{2\beta} \left[F(elev)\right]^2 f(T) \ , \quad \text{..... (351-8)}$$

where Q_2 and β, are constants. The temperature behavior is the same as for the meters in the fine modules, but the pressure/elevation relationship is different. We can use Equation 351-7b with the limitation that the a parameter will vary with site elevation. This is acceptable as long as we perform the calibration at the sampling site. The procedures are significantly simplified by using the same parameterized equation for all orifice meters. Note that the b parameter is approximately 1.0 for the PM10 meter, compared to 0.5 for the fine modules.

4.5.1.4 Pressure-Elevation Relationship

The ambient pressure enters into the equations for UCD audit devices and the system magnehelic as the square root of the pressure. Because of the difficulties of measuring the ambient pressure at each sample change, we have chosen to use an average pressure based on the elevation of the site. The actual pressure is used only in calibrating the audit devices at Davis.

Based on the 1954 tables of Treworth, the pressure at an elevation Z feet can be expressed by

$$P = P_o \exp\left[-\left\{\frac{Z}{27674} + \left(\frac{Z}{87317}\right)^2\right\}\right], \qquad (351\text{-}9)$$

where P_o is the standard pressure at sea level.

It is convenient to define an elevation factor that is the square root of the pressure at sea level divided by the pressure at the site. This factor is expressed as

$$F(elev) = \sqrt{\frac{P_0}{P(site)}} = \exp\left[\frac{1}{2}\left\{\frac{Z}{27674} + \left(\frac{Z}{87317}\right)^2\right\}\right] \quad \text{..... (351-10)}$$

The values of nominal P and F(elev) as a function of elevation and for each site are given in Tables 351-2 and 351-2.

Table 351-2. Elevation Factor *vs*. Elevation

elev	F(elev)	P	elev	F(elev)	P	elev	F(elev)	P
0	1.000	29.92	4000	1.076	25.84	8000	1.160	22.22
100	1.002	29.81	4100	1.078	25.74	8100	1.163	22.14
200	1.004	29.70	4200	1.080	25.65	8200	1.165	22.05
300	1.005	29.60	4300	1.082	25.55	8300	1.167	21.97
400	1.007	29.49	4400	1.084	25.46	8400	1.169	21.88
500	1.009	29.38	4500	1.086	25.36	8500	1.172	21.80
600	1.011	29.28	4600	1.088	25.27	8600	1.174	21.72
700	1.013	29.17	4700	1.090	25.17	8700	1.176	21.63
800	1.015	29.07	4800	1.092	25.08	8800	1.178	21.55
900	1.016	28.96	4900	1.094	24.99	8900	1.181	21.47
1000	1.018	28.85	5000	1.096	24.89	9000	1.183	21.38
1100	1.020	28.75	5100	1.098	24.80	9100	1.185	21.30
1200	1.022	28.64	5200	1.100	24.71	9200	1.187	21.22
1300	1.024	28.54	5300	1.103	24.61	9300	1.190	21.14
1400	1.026	28.44	5400	1.105	24.52	9400	1.192	21.06
1500	1.028	28.33	5500	1.107	24.43	9500	1.194	20.98
1600	1.030	28.23	5600	1.109	24.34	9600	1.197	20.90
1700	1.031	28.13	5700	1.111	24.25	9700	1.199	20.82
1800	1.033	28.02	5800	1.113	24.16	9800	1.201	20.73
1900	1.035	27.92	5900	1.115	24.07	9900	1.204	20.65
2000	1.037	27.82	6000	1.117	23.97	10000	1.206	20.57
2100	1.039	27.72	6100	1.119	23.88	10200	1.211	20.42
2200	1.041	27.62	6200	1.121	23.79	10400	1.215	20.26
2300	1.043	27.51	6300	1.123	23.70	10600	1.220	20.10
2400	1.045	27.41	6400	1.126	23.62	10800	1.225	19.94
2500	1.047	27.31	6500	1.128	23.53			
2600	1.049	27.21	6600	1.130	23.44	11000	1.230	19.79
2700	1.050	27.11	6700	1.132	23.35	11200	1.234	19.64
2800	1.052	27.01	6800	1.134	23.26	11400	1.239	19.48
2900	1.054	26.91	6900	1.136	23.17	11600	1.244	19.33
						11800	1.249	19.18
3000	1.056	26.81	7000	1.138	23.08			
3100	1.058	26.72	7100	1.141	23.00	12000	1.254	19.03
3200	1.060	26.62	7200	1.143	22.91	12200	1.259	18.88
3300	1.062	26.52	7300	1.145	22.82	12400	1.264	18.73
3400	1.064	26.42	7400	1.147	22.74	12600	1.269	18.59
3500	1.066	26.32	7500	1.149	22.65	12800	1.274	18.44
3600	1.068	26.23	7600	1.152	22.56			
3700	1.070	26.13	7700	1.154	22.48	13000	1.279	18.29
3800	1.072	26.03	7800	1.156	22.39			
3900	1.074	25.94	7900	1.158	22.31			

Table 351-3. Elevation Factor *vs.* Site

site	name of site	feet	F(elev)	nom P
ABBO1	Abbotsford	0	1.000	29.92
ACAD1	Acadia	420	1.008	29.47
BADL1	Badlands	2493	1.046	27.32
BAND1	Bandelier	6500	1.128	23.53
BIBE1	Big Bend	3500	1.066	26.32
BLIS1	Bliss State	6700	1.132	23.35
BOWA1	Boundary Waters	1700	1.031	28.13
BRCA1	Bryce Canyon	8440	1.170	21.85
BRID1	Bridger	8000	1.160	22.22
BRIG1	Brigantine	50	1.001	29.87
BRLA1	Brooklyn Lake	10,300	1.213	20.34
CANY1	Canyonlands	5950	1.116	24.02
CHAS1	Chassahowitzka	0	1.000	29.92
CHIL1	Chilliwack	30	1.001	29.89
CHIR1	Chiricahua	5400	1.105	24.52
CORI1	Columbia River	300	1.004	29.60
CRLA1	Crater Lake	6500	1.128	23.53
CRMO1	Craters of Moon	5900	1.115	24.07
DENA1	Denali	2100	1.039	27.72
DEVA1	Death Valley	410	1.007	29.48
DOLA1	Dome Land	2950	1.055	26.86
DOSO1	Dolly Sods	3800	1.072	26.03
EVER1	Everglades	0	1.000	29.92
GICL1	Gila	5840	1.114	24.12
GLAC1	Glacier	4500	1.086	25.36
GRBA1	Great Basin	6800	1.134	23.26
GRCA1	Grand Canyon	7100	1.141	23.00
GRGU1	Great Gulf	1350	1.025	28.49
GRSA1	Great Sand Dunes	8200	1.165	22.05
GRSM1	Great Smoky Mtns	2650	1.050	27.16
GUMO1	Guadalupe Mtns	5400	1.105	24.52
HALE1	Haleakala	3800	1.072	26.03
HAVO1	Hawaii Volcanoes	4100	1.078	25.74
INGA1	Indian Gardens	3800	1.072	26.03
JARB1	Jarbidge	6200	1.121	23.79
JEFF1	Jefferson	920	1.017	28.94
LAVO1	Lassen Volcanic	5900	1.115	24.07
LOPE1	Lone Peak	6200	1.121	23.79
LYBR1	Lye Brook	3250	1.061	26.57
MACA1	Mammoth Cave	750	1.014	29.12
MALO1,2	Mauna Loa	11,150	1.233	19.67
MEVE1	Mesa Verde	7210	1.143	22.90
MOOS1	Moosehorn	100	1.002	29.81
MOZI1	Mount Zirkel	10,560	1.123	19.33
MORA1	Mount Rainier	1430	1.026	28.41
OKEF1	Okefenokee	50	1.001	29.87
PEFO1	Petrified Forest	5500	1.107	24.43
PINN1	Pinnacles	1040	1.019	28.81
PORE1	Point Reyes	125	1.002	29.79
PMRF1	Proctor Maple	1310	1.024	28.53
REDW1	Redwood	760	1.014	29.11
ROMA1	Cape Romain	0	1.000	29.92
ROMO2	Rocky Mountain	8950	1.182	21.43
SAGO1	San Gorgonio	5618	1.109	24.32
SAGU1	Saguaro	3080	1.058	26.74
SALM1	Salmon	9100	1.185	21.30
SAWT1	Sawtooth	6490	1.128	23.53
SCOV1	Scoville	4930	1.095	24.96
SHRO1	Shining Rock	5260	1.102	24.65
SEQU1	Sequoia	1800	1.033	28.02
SHEN1	Shenandoah	3600	1.068	26.23
SIPS1	Sipsey	600	1.011	29.28
SNPA1	Snoqualamie	3600	1.068	26.23
SOLA1	So Lake Tahoe	6250	1.122	23.75
SULA1	Sula	6250	1.122	23.75
THSI1	Three Sisters	2850	1.053	26.93
TONT1	Tonto	2600	1.049	27.21
UPBU1	Upper Buffalo	2300	1.043	27.51
VIIS1	Virgin Islands	150	1.003	29.76
WHRI1	White River	11,220	1.234	19.64
VOYA1	Voyaguers	1140	1.021	28.71
WASH1	Washington D.C.	30	1.001	29.89
WEMI1	Weminuche	9050	1.184	21.34
YELL1	Yellowstone	7744	1.155	22.44
YOSE1	Yosemite	5300	1.103	24.61

4.5.1.5 Calibration of Audit Devices

The reference flow rate is provided by a spirometer located in the sampler laboratory at UCD. The spirometer measurements are verified by a dry gas meter monitoring the exhaust to the calibration pump. Taking the logs of Equation 351-7A, the flow rate equation for the audit device is

$$\log(Q) = a_o + \log\sqrt{\left(\frac{29.92}{P}\right)\left(\frac{T+273}{293}\right)} + b_o * \log(M_o) \quad \text{..... (351-11)}$$

The log of the meter reading, M_o, is regressed against the log of the flow rate for a set of four flow rates covering the normal range of the device. The constants relative to the nominal sea level pressure (29.92) and 20°C are calculated using

$$a_c = \text{intercept} - \log\sqrt{\left(\frac{29.92}{P}\right)\left(\frac{T+273}{293}\right)} \qquad b_o = \text{slope} \quad \text{..... (351-12)}$$

4.5.1.6 Nominal Flow Rate Equation

In order to have a mean annual flow rate of 22.8 L/min at 15°C, the critical orifices are adjusted to provide a flow rate of 23 L/min at 20°C with a typical filter in the cassette. For the Wedding PM10 inlet the nominal flow rate is set at 19.1 L/min at 20°C, while for the Sierra-Anderson PM10 inlet is set at 17.8 L/min. Using Equation 351-7b, the audit device flow rate at the site and 20°C is given by

$$Q_o = 10^{a_0} M_o^{b_0} F(\text{elev}) = 23.0 \text{ L / min} \quad \text{..... (351-13)}$$

The desired reading on the audit device is

$$M_o = \left(\frac{23}{F(\text{elev})}\frac{1}{10^{a_0}}\right)^{1/b_0} \quad \text{..... (351-14)}$$

4.5.1.7 Flow Rate Equation for the System Vacuum Gauge

The measurement by the vacuum gauge is based on the equation for the critical orifice, Equation 351-2):

$$Q = Q_O * \left(1 - \frac{\Delta P}{P}\right) * f(T) \quad \text{.....}$$

We can redefine the Q_O constant to include the elevation factor:

$$Q = Q_3 * \left(1 - \frac{\Delta P}{P}\right) * f(T)\, F(\text{elev}) \text{ , } \quad \text{..... (351-15)}$$

where Q_3 is another constant. We can write this in terms of parameters c and d as

$$Q = c + d*G *f(T) F(elev) \quad \text{(351-16)}$$

The parameter d is negative. The parameters will be independent of temperature, but not independent of pressure. That is, they would change if the sampler were moved to a new location. The form of this equation was chosen to keep it parallel to that of the system orifice meter.

4.5.1.8 Calibration of the System Orifice Meter and Vacuum Gauge

A four point calibration is made of the system orifice meter and the vacuum gauge at the site using an audit device to determine the flow rate at the inlet. The equations for the flow rate from the audit device (Q_0), the system orifice meter (O_m), and the vacuum gauge (Q_g), all relative to sea level and 20°C are:

$$Q_o = 10^{a_0} M_o^{b_0} \quad \text{(351-17)}$$

$$Q_m = 10^{a} M^{b} \quad \text{(351-18)}$$

$$Q_g = c + d * G \quad \text{(351-19)}$$

For each of the four points, Q_0 is calculated using Equation 351-17. For the system orifice meter, the log of Q_0 is regressed against the log of M: a is the intercept and b is the slope. For the vacuum gauge Q_0 is linearly regressed with G: c is the intercept and d is the slope.

In the one point mail audit, M_0, M, and G are recorded for both filters in each module and used to calculate the three flow rates relative to sea level and 20°C.

4.5.2 Determination of Concentration, Artifacts and Precision

The following section is a discussion of the equations used to determine aerosol concentration, both the sum and its parts, the artifacts produced by the analysis and analytical precision provided bye the analysis technique. They are broken into the following sections:

Artifact (4.5.2.1);
Verification by Distributions (4.5.2.2);
Definitions of Variables (4.5.2.3);
Concentration (4.5.2.4);
Volume (4.5.2.5);
Analytical Precision (4.5.2.6);
Gravimetric Mass (4.5.2.7);
PIXE, XRF, and PESA Analysis (4.5.2.8);
Ion, Carbon, and SO_2 Analysis (4.5.2.9);
Optical Absorption (4.5.2.10)

4.5.2.1 Artifact

Artifact is defined as any increase or decrease of material on the filter that positively or negatively biases the measurement of ambient concentration. The five major types of artifact are

- contamination of the filter medium;
- contamination acquired by contact with the cassettes or in handling;
- adsorption of gases during collection that are measured as particles;
- volatilization during collection and in handling;
- fall-off during handling after collection.

The first three are positive artifacts and the last two negative. The first contamination artifact is determined by analysis of laboratory blanks. The sum of the two contamination artifacts is determined by analysis of dynamic field blanks (DFB's). These are handled as normal filters, except that no air is drawn through. The adsorption artifact on quartz filters is determined by analysis of secondary filters. The assumption is that the first filter collects all of the particles and does not significantly remove the relevant gases. The adsorbed gas appears as high temperature organic. Comparison between quartz secondary and blank filters indicates that some of the low temperature artifact acquired in handling is volatilized during collection. There appears to be some adsorption of SO_2 on the nylon filter at some sites; for this reason we do not include the nylon sulfate concentrations in the public data base.

We do not correct for the two negative artifact types, volatilization and fall-off. The measured low temperature organics may be much less than in the atmosphere because of volatilization of particles during the remainder of the sampling. We assume that any volatilization of nitrate and chlorine from nylon is not significant. The fine mass on the Teflon filter will be underestimate the ambient mass concentrations in high nitrate areas because some nitrates collected on Teflon will volatilize.

4.5.2.2 Verification by Distributions

The blanks and secondary filters may not always provide reasonable values for the artifact. In order to verify an estimate from field blanks, we examine the distribution of values for ambient samples in two ways. We first examine the minimum of the ambient values for a large set of samples. If we can reasonably assume that the ambient mass of a given variable is occasionally much less than the artifact, then the minimum measured values of the ambient samples should equal the artifact. To avoid statistical problems, we often examine the 1% level, rather than the actual minimum.

We also examine the intercepts of regression plots of the variable with concentrations of related variables that have no problems with artifact subtraction.

4.5.2.3 Definitions of Variables

Variables calculated prior to sample measurement:

B = artifact mass (ng/filter) = mean of the DFB's or secondary filters
σ_{dfb} = standard deviation of the DFB's or secondary filters used to determine B
σ_a = component of analytical precision that is a constant mass per filter.
f_a = component of analytical precision that is a constant fraction. f_a
f_v = fractional volume precision = fractional flow rate precision

Variables measured or calculated with each sample:

A = mass measured on real sample (ng/filter)
V = volume (m^3)
area = area of deposit on the filter (cm^2) , determined from the mask size
f_s = analytical precision associated with counting statistics, expressed as fraction
c = concentration (ng/m^3)
$\sigma(c)$ = precision of c (ng/m^3)

4.5.2.4 Concentration

The mass of material on the filter is equal to the difference between the mass measured on the sample and the artifact determined from field blanks and secondary filters. The concentration equals this number divided by the volume:

$$c = \frac{A - B}{V} \quad \text{..... (351-20)}$$

4.5.2.5 Volume

The volume is the product of the average flow rate and the sample duration. The sample duration is determined using an elapsed time indicator based on line frequency. The actual time of start and stop is determined by the clock controller using an internal quartz crystal. The fractional precision of the volume is the quadratic sum of the fractional precisions of flow rate and duration. Since the fractional precision of the duration is always much smaller than that of the flow rate, it can be safely neglected.

The flow rate is measured before and after the collection each using two independent methods. The first method measures the pressure drop across the cyclone using a magnehelic and employs the standard measuring orifice equation. The second method measures the pressure drop across the filter and employs the equation for flow through a critical orifice. The equations for flow rate are given earlier in this document. The average flow rate is normally an average of the magnehelic flow rates before and after collection. If the magnehelic readings are determined to be in error, then the gauge measurements are used.

The precision in the average flow rate has two components: the precision in the measured values and the uncertainty in assuming that the average flow rate during collection equals the average of the flow rates measured before and after collection. The precision in a measured value is less than 3%, as estimated from internal and third-party audits. Most audits indicate that the total precision/accuracy of the difference between an audit and an IMPROVE measurement is approximately 3%. Since the precisions of most audit devices are 2-3%, the IMPROVE flow rate precision must be less than 3%.

The second component of the precision is present because all flow control devices introduce uncertainty. A critical orifice device is extremely reliable, avoiding large errors at extreme temperatures, but does allow small variations in flow rate with temperature. A difference in average temperature during the sampling period from the average temperatures before and after collection will produce an incorrect value of flow rate. Suppose both change days (Tuesdays) are colder than a sample day (e.g. Saturday). If the 24-hour mean temperature were 10°C higher than the average of the two measured temperatures, than the error in average flow rate would be 2%. We allow such unusual conditions by using a conservative value for the precision in the volume of 3%. This value has been used in all calculations for the IMPROVE sampler. Calculating site-specific or seasonal precisions would complicate the calculations without significantly changing the overall precision estimate of the concentrations.

4.5.2.6 Analytical Precision

1. Counting Statistics

   There will be uncertainty associated with counting statistics whenever the measurement is based on the number of counts from a detector. Gravimetric and IPM analyses do not involve counting statistics. We are not provided the information on counting statistics for

ion chromatography and carbon combustion. Counting statistics are generally negligible for ion chromatography. They may not be negligible for carbon combustion, but we assume that any statistical precision is accounted for in the constant portion of the non-statistical precision. However, the statistical precision must be included for PIXE, XRF, and PESA because of a relatively large background in the spectra and the absence of direct artifact subtraction. This will be discussed in more detailed in the section on PIXE.

2. Non-statistical Analytical Precision

   For simplicity we will assume that the non-statistical component of the analytical precision may consist of a constant mass/filter (σ_a and a constant fraction (f_a). Theory indicates that some methods, such as gravimetric analysis, have only a σ_a component. The constant fraction form (f_a) is appropriate for uncertainty associated with normalization and calibration. In x-ray systems, f_a represents the uncertainty in normalizing each analysis to an incident beam intensity. In ion chromatography f_a includes the precision in preparing an aliquot. X-ray methods have only a f_a component. For ion chromatography and carbon combustion we will assume both components are present.

3. The total analytical precision in the measured value A (mass/filter) is given by

$$[\sigma(A)]^2 = \sigma_a^2 + (A*f_a)^2 + (A*f_s)^2 \quad \text{..... (351-21)}$$

4. Calculation of Factors for Analytical Precision

   We determine the two non-statistical components, σ_a and f_a, from replicate analyses. We will assume that for each replicate pair the difference is produced by the three factors of Equation 351-21.

   For the elemental analyses, where σ_a is zero, the difference is produced by f_a and f_s. The f_a factor is determined from elements in which the statistical factor is negligible. For PIXE we chose sulfur for sites where there is always abundant sulfur and for XRF we choose iron. In both cases, f_s is zero. Historically, f_a has historically equaled 4% for S by PIXE and for Fe by XRF. Rather than allow this value to vary each season based on the individual analysis run, we have used 4% throughout.

   For ion chromatography and carbon combustion we assume each measurement is given by Equation 351-21 with f_s=0. For each pair of replicate analyses we calculate M = mean and P = difference /$\sqrt{2}$. The relationship between P and M is

$$P^2\left[1-\left(\frac{f_a}{2}\right)^2\right] = \sigma_a^2 + f_a^2 * M^2 \quad \text{..... (351-22)}$$

   The term in brackets is always close enough to 1.00 to justify setting it equal to 1. To to calculate σ_a and f_a , P is plotted against M and the best values are obtained by examining

the regions of low and high M. At low M, σ_a = P. At high M, f_a equals the slope. This approach has the added feature of verifying the validity of separating the analytical precision into the two factors.

4.5.2.7 Gravimetric Mass

In the case of gravimetric analysis, the analytical precision is independent of the magnitude of the measured value, so that both f_a and f_s are zero. Thus, the analytical precision in ng/filter, σ_a, is the same for all samples, including DFB's.

The standard deviation of the DFB's may be expressed as the sum of the precision in the artifact and the precision in the analysis.

$$\sigma_{dfb}^2 = [\sigma(B)]^2 + \sigma_a^2 \quad \text{(351-23)}$$

The precision in the artifact-corrected mass is the sum of the precision of the measurement, σ_a, and the precision in B and is given by

$$[\sigma(A-B)]^2 = \sigma_a^2 + [\sigma(B)]^2 \quad \text{(351-24)}$$

Thus, the precision in the difference (A-B) is equal to the standard deviation in the DFB's

$$\sigma(A-B) = \sigma_{dfb} \quad \text{(351-25)}$$

The precision in the concentration may be written as

$$[\sigma(c)]^2 = \left(\frac{\sigma_{dfb}}{V}\right)^2 + (f_v * c)^2 \quad \text{(351-26)}$$

We define the minimum detectable limit as the concentration that is equal to 2σ. The exact expression is given by

$$mdl = \left(2\frac{s_{dfb}}{V}\right)\left(\frac{1}{\sqrt{1-4f_v^2}}\right) \quad \text{(351-27)}$$

The right- term equals 1.002 for f_v=0.03. The difference from 1.00 is negligible compared to the uncertainties in σ_{dfb} and V. We will use the simpler expression

$$mdl = 2\frac{\sigma_{dfb}}{V} \quad \text{(351-28)}$$

4.5.2.8 PIXE, XRF, and PESA Analysis

In PIXE, XRF, and PESA, the spectral background for a sample is estimated using a spectrum of a blank Teflon filter. This procedure removes any contaminants, if present. These spectra of blank filters indicate that any elemental artifact is extremely small. Therefore the

concentration is calculated using B=0. We use a variation of Equation 351-20, because PIXE, XRF, and PESA determine mass per unit area rather than mass per filter. This areal density in ng/cm^2 is proportional to the number of counts in the peak, with the proportionality factor depending on the element, the number of protons, and the detector live time. The spectral analysis program is provided the ratio of deposit area divided by sample volume. The concentration is calculated using

$$c = k * N * \frac{area}{V} , \quad \text{(351-29)}$$

where area is the area of deposit on the filter, N is the number of counts in the peak, and k is a constant depending on the element, the number of protons, and the detector live time.

None of the three methods have a constant component to the precision, so that $\sigma_a=0$. All have constant fractional components, (f_a), associated with normalizing to the incident beam. The value of f_a is measured every analytical session using replicate analyses for elements with negligible statistical precision. It has never varied significantly from 4%. We have maintained a constant value of $f_a=0.04$ in the data processing since 1988.

Measurements by all three methods have a statistical component to the precision, (f_s), based on the number of counts in the peak and in the background under the peak. Assuming a Poisson distribution, N counts in the peak, and N_b background counts under the peak, the fractional statistical precision is given by

$$f_s^2 = \frac{1}{N}\left(1+2\frac{N_b}{N}\right) \quad \text{(351-30)}$$

The precision of the concentration is given by

$$[\sigma(c)]^2 = c^2 * (f_s^2 + f_a^2 + f_v^2) \quad \text{(351-31)}$$

The precision is calculated separately for each variable at the time of spectral analysis using f_a = 0.04 and f_v = 0.03. The quadratic sum of these two is 0.05. At small concentrations the statistical term is dominant, while at large concentrations the precision approaches 5%. For sulfur, the average precision for all sites and seasons is slightly larger than 5%.

The minimum detectable limit for each PIXE variable is calculated from the background in the spectrum at the location of the peak and the relationship between counts and concentration for that peak. The mdl is defined as the concentration at which the number of valid counts equals 3.3 times the square root of the background counts under the peak. The mdl defines the upper limit that a variable can be reliably observed in the spectrum, although it is possible to find peaks with concentrations slightly below the mdl. At the mdl, the analytical precision is approximately 50% of the mdl. The mdl is calculated separately for each variable at the time of spectral analysis.

4.5.2.9 Ion, Carbon and SO_2 Analysis

The equations for these three methods are the same, except for SO_2, where the concentrations are multiplied by 2/3 to convert from SO_4 to SO_2. The methods are characterized by significant artifact and unknown statistical precision.

The standard deviation of the DFB's or secondary filters includes the precision in the artifact and the analytical precision. (As in the case of gravimetric analysis, we do not equate the precision in the artifact with the standard deviation of the DFB's.) The standard deviation is a quadratic sum of the precision of the artifact B, the constant analytical precision, and the fractional analytical precision:

$$\sigma_{dfb}^2 = [\sigma(B)]^2 + \sigma_a^2 + [f_a * B]^2 \quad \text{(351-32)}$$

The precision of the mass/filter of the sample is

$$[\sigma(A)]^2 = \sigma_a^2 + [f_a * A]^2 \quad \text{(351-33)}$$

The precision of the difference (A-B) is obtained by quadratically adding the precisions of A and B,

$$[\sigma(A-B)]^2 = [\sigma(A)]^2 + [\sigma(B)]^2 \quad \text{(351-34)}$$

The precision of the concentration is therefore given by

$$\left[\sigma(c)\right]^2 = \left[\frac{\sigma(A-B)}{V}\right]^2 + \left[f_v * c\right]^2 = \left[\frac{\sigma(B)}{V}\right]^2 + \left[f_a * \frac{A}{V}\right]^2 + \left[f_v * c\right]^2 \quad \text{(351-35)}$$

This can be written in terms of the constants as

$$\left[\sigma(c)\right]^2 = \left[\frac{\sigma_{dfb}}{V}\right]^2 + \left(\frac{2B}{V}\right) * f_a^2 * c + \left(f_a^2 + f_v^2\right) * c^2 \quad \text{(351-36)}$$

Note that the constant analytical precision, σ_a, does not appear in Equation 351-36. This portion of the precision is included indirectly in σ_{dfb}.

For small c, the first term in Equation 351-36 is dominant, while for large c, the third term is dominant. The second term is never dominant; the maximum contribution for most parameters is less than 10%.

The minimum detectable limit is defined as the concentration that is twice the precision. Solving Equation 351-36 for the concentration gives

$$\text{mdl} = \left(2\frac{\sigma_{dfb}}{V}\right)\left(\frac{\sqrt{1-h-g}+g}{1-h}\right) \quad \text{.....(351-37)}$$

where $g = \left(\frac{2B}{\sigma_{dfb}}\right) f_a^2 \qquad h = 4(f_a^2 + f_v^2)$.

Retaining the second order terms would increase the estimate of the mdl less than 2% for ion chromatography and organic carbon. The simplified form that drops second order terms is used in the data processing:

$$\text{mdl} = 2\frac{\sigma_{dfb}}{V} \quad \text{.....(351-38)}$$

4.5.2.10 Optical Absorption

The calculation of the coefficient of absorption does not follow Equation 351-20. The modified Laser Integrating Plate Method (LIPM) system has a 2" sphere to measure reflected light and an integrating to measure a fraction of the transmitted light. The exposed side of the filter is always placed away from the source, so that the light first passes through the Teflon. The system is calibrated by reference to our 6" research integrating sphere. The LIPM sphere detector is adjusted to give the same value of R for a reference filter as the research sphere in the reflectance mode. The LIPM plate detector is adjusted to give the same value of T as the research sphere in the transmittance mode. In the data processing system, the absorption measured on the filter is labeled LRNC for 'laser not corrected'. (The ambient coefficient is considered a composite variable and is labeled BABS.) For area in cm^2 and volume in m^3, the equation for the uncorrected coefficient of absorption in 10^{-8} m^{-1} is

$$\text{LRNC} = \left(\frac{\text{area}}{V}\right) 10^4 \ln\left(\frac{1000-R}{T}\right) \quad \text{.....(351-39)}$$

No measurement of the clean filter is needed because Teflon does not absorb light. Because of layering effects inherent in collecting particles on a filter, the absorption measured on the filter (LRNC) is less than the ambient absorption (BABS). The parameter BABS is discussed in section 4.5.3. The uncertainty in LRNC is determined by replicate measurements of ambient filters.

$$\left[\sigma(\text{LRNC})\right]^2 = \left(\frac{\text{area}}{V} * 225.\right)^2 + \left(f_v * \text{LRNC}\right)^2 \quad \text{.....(351-40)}$$

Note that because of the relative large uncertainty in the mass correction, this uncertainty in LRNC is generally much less than the final uncertainty in BABS.

The minimum detectable limit is defined as twice the precision in the measurement for a sample with low absorption. The approximate expression for the mdl in 10^{-8} m^{-1} is then

$$mdl = \frac{area}{V} * 450 \quad \text{(351-41)}$$

For a typical filter with a collection area of 2.2 cm^2, the mdl is approximately 30 10^{-8} m^{-1} or 0.3 $(Mm)^{-1}$.

4.5.3 Equations of Composite Variables

The following composite variables are combinations of the measured concentrations of particles collected on the fine filters. These are used in the level II validation procedures and in the seasonal summaries.

The precision of each concentration is determined along with the value of the concentration and the minimum detectable limit (mdl) of each concentration. In our calculations of the precision of the composite variables, we will assume that the component concentrations are independent and the multiplicative factors have no uncertainty. The independence assumption is not strictly valid for many composites because of common factors, such as volume. However, the effect on the overall precision is too small to warrant the more complicated calculations. The following sections are divided by composite. They are as follow:

Sulfate by PIXE (S3) and Ammonium Sulfate (NHSO) (4.5.3.1);
Ammonium Nitrate (NHNO) (4.5.3.2);
Soil (4.5.3.3);
Non-soil Potassium (KNON) (4.5.3.4);
Light-Absorbing Carbon (LAC) (4.5.3.5);
Ambient Coefficient of Absorption (BABS) (4.5.3.6);
Organics by Carbon (OMC) (4.5.3.7);
Organics by Hydrogen (OMH) (4.5.3.8);
Reconstructed Mass from the Teflon Filter (RCMA) (4.5.3.9);
Reconstructed Mass using Carbon Measurements (RCMC) (4.5.3.10)

4.5.3.1 Sulfate by PIXE (S3) and Ammonium Sulfate (NHSO)

Sulfur is predominantly present as sulfate. To compare the sulfur by PIXE and the sulfate by ion chromatography, the PIXE concentration is multiplied by 3.0. This composite is labeled S3.

The sulfate is generally present as ammonium sulfate, $(NH_3)_2SO_4$, although it can be present as ammonium bisulfate, $(NH_3)HSO_4$, sulfuric acid, H_2SO_4, and, in marine areas, as sodium sulfate, $NaSO_4$. In many of these cases, the particle will include associated water, but w omit this from the calculation. In order to simplify the calculation we will assume all the sulfur is present as ammonium sulfate. The concentration and precision is given by:

$$NHSO = 4.125 * S \quad \text{(351-42)}$$
$$\sigma(NHSO) = 4.125 * \sigma(S) \quad \text{(351-43)}$$

(Strictly, the factor should be 4.121, but 4.125 is the traditional value.) If S is below the mdl, both S and $\sigma(S)$ are set equal to mdl/2. For ammonium bisulfate, sulfuric acid, and sodium sulfate the factors are 3.59, 3.06, and 4.43, respectively. In the first two cases, the actual dry mass associated with sulfate will be less than NHSO, and in the third case, more.

4.5.3.2 Ammonium Nitrate (NHNO)

This composite is the total dry concentration associated with nitrate, assuming 100% neutralization by ammonium. For all sites, we define the ammonium nitrate concentration and precision by:

$$NHNO = 1.29 * NO_3^- \quad \text{..... (351-44)}$$

$$\sigma(NHNO) = 1.29 * \sigma(NO_3^-) \quad \text{..... (351-45)}$$

4.5.3.3 SOIL

The soil component consists of the sum of the predominantly soil elements measured by x-ray analysis, plus oxygen for the normal oxides (Al_2O_3, SiO_2, CaO, K_2O, FeO, Fe_2O_3, TiO_2), plus a factor for other compounds, such as MgO, Na_2O, water, and CO_2. The following assumptions are made:

- We will assume that the Fe is split equally between FeO (oxide factor of 1.29) and Fe_2O_3 (oxide factor of 1.43), giving an overall Fe oxide factor of 1.36.
- Fine K has a non-soil component from smoke. Based on the K/Fe ratio for average sediment (Handbook of Chemistry and Physics) of 0.6, we use 0.6*Fe as a surrogate for soil K. With the oxide factor of K, this is increases the factor for Fe from 1.36 to 2.08.
- Because aluminum has not always been detected with as high a frequency as the other major soil elements, we have eliminated Al from the soil parameter. Fortunately, the correlation between Al and Si is excellent for all sites, with a constant ratio of Al/Si of 0.45. With the oxide factors for Al_2O_3 and SiO_2 the multiplicative factor for Si increases from 2.14 to 2.99 . The only exception is Virgin Islands, where the Al/Si ratio is 0.60; the soil parameter is then low by 6%.
- The oxide forms of the soil elements account for 86% of average sediment; in order to obtain the total mass associated with soil, the final factors are divided by 0.86 (handbook of Chemistry and Physics. The final equations for fine soil concentrations and precision are:

$$SOIL = 2.20*Al + 3.48*Si + 1.63*Ca + 2.42*Fe + 1.94*Ti \quad \text{(351-46)}$$

$$[\sigma(SOIL)]^2 = [3.48*\sigma(Si)]^2 + [1.63*\sigma(Ca)]^2 + \ldots \quad \text{(351-47)}$$

The soil variable is calculated for all valid PIXE analyses. If an element is below the mdl, the concentration and precision are both assumed to be equal to mdl/2. The soil variable is always positive.

4.5.3.4 Non-soil Potassium (KNON)

Non-soil K is the measured fine K minus the soil K estimated from Fe. Non-soil K is a qualitative tracer of smoke, but may not be a quantitative measure of the mass of smoke aerosol. The problem is that the ratio of K / smoke mass may change as the aerosol ages. Particulate smoke K is probably produced by transformation of volatilized K, and appears to be on smaller particles than most smoke mass. When close to the source, the particulate K may not have time to form. For long transport, most other smoke mass may settle out more than K mass. The concentration and precision of KNON are:

$$KNON = (K - 0.6*Fe) \quad \text{(351-48)}$$

$$\sigma^2(KNON) = \sigma^2(K) + [0.6*\sigma(Fe)]^2 \quad \text{(351-49)}$$

The soil factor of 0.6 may vary slightly with site; this will produce a small positive or negative offset for baseline values, when no smoke is present. Therefore, negative values are retained.

KNON is defined for all valid PIXE analyses. If a concentration is less than the mdl, the concentration and precision are assumed to be equal to mdl/2.

4.5.3.5 Light-Absorbing Carbon (LAC)

The concentration of carbon on quartz is determined in seven temperature ranges, plus a correction fraction for pyrolized organic. The light-absorbing component is assumes to be all carbon evolved at 550°C and above after the laser indicates that reflectance has returned to the initial value. The equation for concentration is:

$$LAC = E1 + E2 + E3 - OP \quad \text{..... (351-50)}$$

LAC may be negative. The uncertainty of LAC is not the quadratic sum of the components. Based on replicate measurements, the best estimate of uncertainty is:

$$\sigma(LAC) = \sqrt{(34)^2 + (0.067 * LAC)^2} \ \text{ng/m}^3 \quad \text{..... (351-51)}$$

4.5.3.6 Ambient Coefficient of Absorption (BABS)

BABS has an unusual position in the data base. The uncorrected coefficient of absorption, LRNC, is stored in the internal data base, but is not provided for external users. The external users are only provided with the corrected (or ambient) coefficient.

The first and smallest correction is associated with the integrating plate method. In the integrating plate method any scattering with angles large enough to miss the plate causes an increase in apparent absorption. In order to quantify the effect of the large angle scattering, a series of comparisons were made between the integrating plate system and an integrating sphere system. The integrating sphere system, is somewhat more difficult to use routinely, but eliminates the scattering component. Comparison of the results indicates that approximately 3% of the apparent absorption by LIPM is associated with scattering. The measured coefficient is therefore multiplied by 0.97.

Several tests involving simultaneous measurements of the same atmosphere but with differing mass per unit area (areal density) have shown that it is necessary to correct the values measured on a filter to obtain the proper atmospheric absorption. This is true for both integrating plate and integrating sphere. The correction is small for very lightly loaded samples, but we are constrained to design a sampler primarily for other particle measurements. The hypothesis is that the absorption of particles on a filter is less than the ambient absorption of particles because other particles on the filter can shield a given absorbing particle. A form was chosen that included two exponents of the areal density of particles measured by gravimetric analysis in $\mu g/cm^2$. Note that the effect is observed even if the layering mechanism is not correct. The equation used is

$$R = 0.36 \exp\left(-\frac{\rho t}{22}\right) + 0.64 \exp\left(-\frac{\rho t}{415}\right) \quad \text{..... (351-52)}$$

where the constants were determined by fitting data from independent studies at Davis and Los Angeles.

The equation for the ambient coefficient of absorption in 10^{-8} m^{-1} is derived from the uncorrected coefficient using:

$$BABS = LRNC * \frac{0.97}{R} \quad \text{..... (351-53)}$$

The uncertainty in R is estimated to be 10% of (1-R), based on the precision of the fit for the test data. The equation for the precision of the corrected coefficient of absorption is:

$$\sigma(BABS) = \left(\sigma(LRNC) * \frac{0.97}{R}\right)^2 + \left(0.10 * \frac{1-R}{R} * b\right)^2 \quad \text{..... (351-54)}$$

The minimum detectable limit is defined as twice the precision in the measurement for a sample with low absorption. Although this will vary with the intensity for a clean filter, it is more convenient to use a single intensity of 390 units for a typical clean filter. The expression for the mdl is then approximately

$$mdl(BABS) = mdl(LRNC) * \frac{0.97}{R} \quad \text{..... (351-55)}$$

The concentration of absorbing particles can also be estimated from the coefficient of absorption using the absorption efficient ε in m^2/g. For high temperature elemental carbon, such as diesel emissions, the value of ε is typically 10 m^2/g. Thus the concentration of absorbing carbon in ng/m^3 is numerically equal to BABS in 10^{-8} m^{-1}.

However, the comparison of BABS and the concentration light absorbing carbon, LAC, indicates that the BABS method yields a concentration that is approximately twice that of LAC. The two variables are moderately correlated (r=0.74 for western sites). There are three possible explanations:

- The UCD integrating plate and integrating sphere methods both give values of b_{abs} that are high by a factor of 2.
- The absorption efficient of 10 m^2/g is not appropriate for the low temperature elemental carbon measured at remote sites.
- Some of the organic carbon absorbs light. There is a better relationship if we assume that all carbon evolved at 550°C absorbs light with an absorption efficient of 10 m^2/g.

4.5.3.7 Organics by Carbon (OMC)

The concentration of carbon on quartz is determined in seven temperature ranges, plus a correction fraction for pyrolized organic. The organic component is assumes to be all carbon evolved at 550°C and below in a pure helium environment, plus the pyrolized organic fraction. The equation for concentration is:

$$OMC = 1.4\ (O1 + O2 + O3 + O4 + OP) \quad \text{..... (351-56)}$$

OMC may be negative. The uncertainty of OMC is not the quadratic sum of the components. Based on replicate measurements, the best estimate of uncertainty is:

$$\sigma(OMC) = \sqrt{(168)^2 + (0.05 * OMC)^2} \ \text{ng/m}^3 \quad \text{..... (351-57)}$$

4.5.3.8 Organics by Hydrogen (OMH)

The organic mass can also be calculated from the concentrations of H and S measured on the Teflon filter. The assumptions are:

- All sulfur is present as fully neutralized ammonium sulfate. This is valid at all sites except those in the East with high sulfur, and at marine sites with significant marine sulfate.
- All nitrates and water volatilize during exposure to vacuum, so the PESA hydrogen comes only from sulfates and organics. This assumption is valid at all except those sites in California with such high nitrate concentrations that some hydrogen remains.
- The average organic particle contains 9% hydrogen. That is, we must multiply the organic hydrogen by 11 to estimate total organic mass.

The equations for OMH concentration and precision are:

$$OMH = 11\ (\ H - 0.25 * S\ ) \quad \text{..... (351-58)}$$

$$\sigma^2(OMH) = (11)^2\ [\sigma^2(H) + [0.25 * \sigma(LAC)]^2 \quad \text{..... (351-59)}$$

If either H or S are invalid or not detected (below mdl), then OMH is not calculated. OMH may be negative when the sulfate is large and not fully neutralized.

At sites where the above assumptions are reasonable, the resulting estimate is in good agreement with organic mass by carbon, OMC, except for the multiplicative constant of 11. For all western sites excluding those with high ammonium nitrate and marine sulfur (San Gorgonio, Pinnacles, Point Reyes and Redwood) the correlation is good (r=0.89) and the slope is very close to 0.80. There are two possible explanations for the 80% ratio between OMC and OMH as defined above. One is that the volatile organic hydrogen component is lost in vacuum. The second explanation is that the carbon analytical methods attributes some of the elemental carbon to the organic fraction. Either change shifts the ratio close to 1. At eastern sites the OMH concentration is sometimes much less than OMC, and is occasionally negative. For these samples some of the sulfate is present as sulfuric acid.

4.5.3.9 Reconstructed Mass from the Teflon filter (RCMA)

The reconstructed mass is the sum of sulfate, soil, non-sulfate potassium, salt, elemental carbon, and organic carbon. The only components not included are water and nitrate. A significant fraction (>50%) of the nitrate particles volatilize from the Teflon filter during collection and is not measured by gravimetric analysis. The nitrate measured in the IMPROVE system is collected on nylon filters and do not volatilize during collection. Therefore, we have chosen to exclude the measured nitrate from the reconstructed mass. Nitrate collected on nylon filters should not be included in the reconstructed mass when comparing it to the gravimetric mass on the Teflon filter. However, when estimating the actual ambient mass, one should add $1.29*NO_3^-$ to the reconstructed mass.

We will use two estimates of reconstructed mass: RCMA, based only on the Teflon filter and using BABS/2 for elemental carbon and OMH for organic mass; and RCMC, based partly on the carbon measurements from the quartz filter and partly on measurements from the Teflon filter. The equations for RCMA concentration and precision are:

$$RCMA = 4.125*S + SOIL + 1.4*KNON + 2.5*Na + BABS/2 + OMH \quad \text{(351-60)}$$

$$\sigma^2(RCMA) = [4.125*\sigma(S)]^2 + [\sigma(SOIL)]^2 + [1.4*\sigma(KNON)]^2 + \ldots \quad \text{(351-61)}$$

For RCMA to be calculated, PIXE, PESA, and LIPM must all have valid analyses. The 1.4 factor with KNON ensures consistency with the soil estimate; it exactly compensates for the removal of non-soil K from soil. Thus potassium is included in the sum as K_2O, whether as soil or as smoke. The salt (NaCl) concentration is estimated solely from Na, because some of the chlorine is volatilized from the Teflon filter during collection. If S, Na, or b_{abs} are below the mdl, mdl/2 is used as both concentration and precision. KNON is used as calculated, even if negative. If OMH is negative, a value of zero is used in the sum. RCMA will always be positive.

4.5.3.10 Reconstructed Mass using Carbon Measurements (RCMC)

An alternative estimate is based on organics and elemental carbon from the quartz filter. As in RCMA, the sum does not include water and nitrates. The equation for RCMC is:

$$RCMC = 4.125*S + SOIL + 1.4*KNON + 2.5*Na + LAC + OMC \quad \text{(351-62)}$$

For RCMC to be calculated, PIXE and carbon combustion must both have valid analyses. If LAC or OMC is negative, a value of zero is used. RCMC will always be positive. .

In general, RCMA is preferred during periods of low organic concentrations, such as winter in western United States. RCMC is preferred at sites where the neutralization of sulfate may be less than 100%, at sites with high nitrate, and at marine sites.

4.5.4 Statistical calculation

The following sections deal with statistical equations used through out the quality assurance process. They are divided into the following sections:

Slope and Intercept for Perpendicular Fit (4.5.4.1);
Pair-wise Precision (4.5.4.2);
Pair-wise Chi-Square (4.5.4.3)

4.5.4.1 Slope and Intercept for Perpendicular Fit

The validation procedures include examination of correlation plots between two variables. Because both variables has associated uncertainty, it is necessary to construct the regression line that minimizes the perpendicular deviations of the points from the straight line. To do this it is first necessary to calculate the various means:

$$< x >= \frac{1}{n}\sum_{i=1}^{n} x_i \qquad < y >= \frac{1}{n}\sum_{i=1}^{n} y_i \quad \ldots\ldots\ldots\ldots$$

$$< x^2 >= \frac{1}{n}\sum_{i=1}^{n} (x_i)^2 \qquad < y^2 >= \frac{1}{n}\sum_{i=1}^{n} (y_i)^2 \qquad < xy >= \frac{1}{n}\sum_{i=1}^{n} x_i y_i \quad \ldots\ldots\ldots\ldots (351\text{-}63)$$

The variances are calculated from the means:

$$S_x =< x^2 > -(< x >)^2 \qquad S_y =< y^2 > -(< y >)^2 \qquad S_{xy} =< xy > - < x >< y > \quad \ldots\ldots\ldots (351\text{-}64)$$

The correlation coefficient is

$$r^2 = \frac{(S_{xy})^2}{S_x S_y} \quad \ldots\ldots\ldots\ldots (351\text{-}65)$$

The expression for the slope involves the difference between the x and y variances:

$$S_d = \frac{S_y - S_x}{2} \quad \ldots\ldots\ldots\ldots (351\text{-}66)$$

We will the equation for the line to be y = a+bx. The slope b is given by:

$$\text{slope} = b = \frac{S_d + \sqrt{(S_d)^2 + (S_{xy})^2}}{S_{xy}} \quad \ldots\ldots\ldots\ldots (351\text{-}67)$$

The intercept a is given by:

$$\text{intercept} = a =< y > - b < x > \quad \ldots\ldots\ldots\ldots (351\text{-}68)$$

To calculate the precisions in a and b, we first calculate the parameters f and g:

$$f = \frac{S_y + b^2 S_x}{S_{xy}} \qquad g = f - 2b \quad \text{.....(351-69)}$$

The precision of the slope is:

$$\sigma_b^2 = \frac{fg}{n-2} \quad \text{.....(351-70)}$$

The precision of the intercept is:

$$\sigma_a^2 = \left[< x > \sigma_b \right]^2 + \frac{2g\, S_{xy}}{n-2} \quad \text{.....(351-71)}$$

4.5.4.2 Pair-wise Precision

The pair-wise relative precision is included on the plots for replicate analyses or for the same parameter by different analytical methods. For replicate analyses with negligible statistical or constant precision, this parameter gives the relative analytical precision discussed in section 4.5.2.

For multiple measurements of a single quantity, z, the absolute precision is the standard deviation and the relative precision is the standard deviation divided by the mean. The "unbiased estimate" of the standard deviation is defined as

$$(\text{stdev})^2 = \frac{n}{n-1}\left[< z^2 > - (< z >)^2 \right] \quad \text{.....(351-72)}$$

Suppose there are only two measurements of each quantity, x and y. The standard deviation for this pair is given by Equation 351-72 with n=2:

$$(\text{stdev})^2 = 2\left[\frac{x^2 + y^2}{2} - \left(\frac{x+y}{2} \right)^2 \right] = \frac{1}{2}(x-y)^2 \quad \text{.....(351-73)}$$

If D is the absolute difference $|x-y|$ and M is the mean, the standard deviation and relative precision are:

$$\text{stdev} = \frac{1}{\sqrt{2}} D \qquad P = \frac{1}{\sqrt{2}} \frac{D}{M} \quad \text{.....(351-74)}$$

Suppose there are n such pairs. The overall precision is the root-mean-square of the individual precisions. The absolute precision, P_{abs} is the sum of the individual standard deviations, while the relative precision, P, is the sum of the individual relative precisions:

$$P_{abs}^2 = \frac{1}{2n} \sum_{i=1}^{n} D_i^2 \qquad P^2 = \frac{1}{2n} \sum_{i=1}^{n} \left(\frac{D_i}{M_i} \right)^2 \quad \text{.....(351-75)}$$

These can also be written in terms of the x's and y's as:

$$P_{abs}^2 = \frac{1}{2n}\sum_{i=1}^{n}\left(x_i - y_i\right)^2 \qquad P^2 = \frac{2}{n}\sum_{i=1}^{n}\left(\frac{x_i - y_i}{x_i + y_i}\right)^2 \quad \text{.....(351-76)}$$

4.5.4.3 Pair-wise Chi-Square

The pair-wise goodness-of-fit parameter, χ^2, is also included on the plots for replicate analyses or for the same parameter by different analytical methods. This parameter, compares the differences with the precision of the differences as determined for the precision of x and y included in the data base. It is thus the best method of determining whether the differences are within the predicted precision.

If σ_x and σ_y are the calculated precisions for x and y, the precision of the difference is:

$$\sigma_d^2 = \sigma_x^2 + \sigma_y^2 \quad \text{.....(351-77)}$$

The goodness-of-fit parameter, χ^2, is:

$$\chi^2 = \frac{1}{n}\sum\left(\frac{D}{\sigma_d}\right)^2 = \frac{1}{n}\sum\frac{\left(x_i - y_i\right)^2}{\sigma_x^2 + \sigma_y^2} \quad \text{.....(351-78)}$$

Large values of χ^2 indicate that there are probably sources of difference not included in the estimate of precision.

4.6 Transfer of Data to Final Concentrations Database

The final data set is presented in several ways to the end users. The final database that gets passed onto the masses takes the form of a simple ASCII file. Each ASCII file is designated with a site code and season code to identify the place and season of aerosol data contained within. The following is a short sample of the database that is provided to the end users:

```
*****************************************************************************
*   Use of IMPROVE data requires acknowledgment both of its production by the  *
* Air Quality Group at the University of California at Davis and of its funding*
* by the National Park Service, US Department of Interior.                    *
*****************************************************************************
 ACAD1 06/01/96 0000  24.00  23.6 MF     8386.30    291.50    294.30 NM
 ACAD1 06/01/96 0000   0.00   0.0 BABS    872.95     94.19     87.20 NM
 ACAD1 06/01/96 0000   0.00   0.0 MT    14264.30    467.30    375.40 NM
 ACAD1 06/01/96 0000  24.00  23.6 H       394.81     20.96      3.37 NM
 ACAD1 06/01/96 0000  24.00  23.6 NA      101.20      9.87     12.85 NM
 ACAD1 06/01/96 0000  24.00  23.6 MG        0.00      0.00      7.42 NM
 ACAD1 06/01/96 0000  24.00  23.6 AL       56.37      5.89      4.81 NM
 ACAD1 06/01/96 0000  24.00  23.6 SI      111.95      7.58      3.93 NM
 ACAD1 06/01/96 0000  24.00  23.6 P         0.00      0.00      3.77 NM
 ACAD1 06/01/96 0000  24.00  23.6 S       621.16     32.51      3.59 NM
 ACAD1 06/01/96 0000  24.00  23.6 CL        0.00      0.00      3.42 NM
 ACAD1 06/01/96 0000  24.00  23.6 K        56.63      3.69      2.16 NM
 ACAD1 06/01/96 0000  24.00  23.6 CA       35.42      2.79      1.69 NM
 ACAD1 06/01/96 0000  24.00  23.6 TI        7.18      1.36      1.53 NM
```

```
ACAD1 06/01/96 0000  24.00  23.6 V         0.00      0.00      1.27 NM
ACAD1 06/01/96 0000  24.00  23.6 CR        0.00      0.00      1.04 NM
ACAD1 06/01/96 0000  24.00  23.6 MN        4.11      0.91      0.90 NM
ACAD1 06/01/96 0000  24.00  23.6 FE       34.26      1.82      0.18 NM
ACAD1 06/01/96 0000  24.00  23.6 NI        0.67      0.08      0.10 NM
ACAD1 06/01/96 0000  24.00  23.6 CU        1.08      0.11      0.10 NM
ACAD1 06/01/96 0000  24.00  23.6 ZN        5.44      0.32      0.10 NM
ACAD1 06/01/96 0000  24.00  23.6 AS        2.52      0.29      0.06 NM
ACAD1 06/01/96 0000  24.00  23.6 PB        3.67      0.29      0.09 NM
ACAD1 06/01/96 0000  24.00  23.6 SE        0.32      0.04      0.05 NM
ACAD1 06/01/96 0000  24.00  23.6 BR        3.27      0.20      0.07 NM
ACAD1 06/01/96 0000  24.00  23.6 RB        0.00      0.00      0.10 NM
ACAD1 06/01/96 0000  24.00  23.6 SR        0.32      0.06      0.11 NM
ACAD1 06/01/96 0000  24.00  23.6 ZR        0.39      0.10      0.17 NM
ACAD1 06/01/96 0000  24.00  23.6 MO        0.00      0.00      0.00
ACAD1 06/01/96 0000   0.00   0.0 BSO4   1906.30     69.30     15.10 NM
ACAD1 06/01/96 0000   0.00   0.0 CL-      11.20      3.40      6.70 NM
ACAD1 06/01/96 0000   0.00   0.0 NO2-     -8.30      3.00      6.10 NM
ACAD1 06/01/96 0000   0.00   0.0 NO3-    161.50      9.00     10.80 NM
ACAD1 06/01/96 0000   0.00   0.0 SO2    1626.10    126.30     40.60 NM
ACAD1 06/01/96 0000   0.00   0.0 O1       48.90     58.90     97.00 NM
ACAD1 06/01/96 0000   0.00   0.0 O2      449.70     99.60    101.70 NM
ACAD1 06/01/96 0000   0.00   0.0 O3      673.00     94.20     69.30 NM
ACAD1 06/01/96 0000   0.00   0.0 O4      520.10     75.30     29.10 NM
ACAD1 06/01/96 0000   0.00   0.0 OP      305.90     84.20     26.70 NM
ACAD1 06/01/96 0000   0.00   0.0 E1      535.40     74.10     25.90 NM
ACAD1 06/01/96 0000   0.00   0.0 E2       55.10     31.80     42.00 NM
ACAD1 06/01/96 0000   0.00   0.0 E3       18.40     12.30     15.50 NM
```

The files are placed onto the UCD anonymous FTP site for retrieval by the end user. The site contains a read me file that describes the format the data and file name. It also provides other information relevant to the data set including flags and other comments about the database in general. The following is an excerpt from that file:

The file names contained in the ZIP files on this disk are coded as follows:
****

The filenames are coded:(e.g.ACAD1A1A.D91)
- position 1-5 site code
- position 6-7 sampler type
- position 8 file type (A denotes ASCII database file)
- position 10 season
- position 11-12 year containing the first month of the season

SEASONS:
'A'=SPRING(MAR.-MAY)
'B'=SUMMER(JUNE-AUG.)
'C'=FALL(SEPT.-NOV.)
'D'=WINTER(DEC.-FEB.)

SAMPLER TYPES:
'A1'=IMPROVE

RECORDS ARE WRITTEN ON THE TAPE IN THE FOLLOWING FORMAT:
SITE CODE,SAMPLE DATE,START TIME,DURATION,FLOW RATE,SPECIES,
AMOUNT,ERROR,MINIMUM DETECTABLE LIMIT,SPECIES STATUS
(1X,A5,1X,A8,1X,I4.4,F7.2,F6.1,1X,A4,3F10.2,1X,A2)

If the AMOUNT, ERROR and MINIMUM DDETECTABLE LIMIT are all zero there is no
valid measurement available for that species.

SPECIES STATUS CODES:
'NM'=NORMAL
'QU'=QUESTIONABLE;UNDETERMINED
'QD'=QUESTIONABLE DATA
'AA'=ORGANIC ARTIFACT CORRECTED
'AP'=POSSIBLE ORGANIC ARTIFACT (No correction performed)
' '=NO ANALYSIS AVAILABLE FOR THIS SPECIES

****
From 9/90 through 2/92 we received some Teflon filters with an organic contamination. This artifact influenced only the Hydrogen and Fine Mass measurements in less than 7% of the samples (marked AA). All other measurements of Hydrogen and Fine Mass during this period are marked with a status AP.

SPECIES CODE:
'MF '=FINE MASS(UCD)
'MT '=PM10 MASS(UCD)
'BABS'=OPTICAL ABSORPTION(UCD)
'H   '=HYDROGEN(UCD)
'BSO4'=SULFATE ON NYLON(RTI,GGC)
'NO2-'=NITRITE(RTI,GGC)
'NO3-'=NITRATE(RTI,GGC)
'CL- '=CHLORIDE(RTI,GGC)
'SO2 '=SULFUR DIOXIDE(DRI)
'OCLT'=ORGANIC CARBON(LOW TEMP)
'OCHT'=ORGANIC CARBON(HI TEMP)
'ECLT'=ELEMENTAL CAR.(LOW TEMP)
'ECHT'=ELEMENTAL CAR.(HI TEMP)
ALL OTHER SPECIES ARE ELEMTAL VALUES FROM UCD PIXE ANAYSIS.

ALL VALUES ARE IN NANOGRAMS/CUBIC METER EXCEPT FOR 'BABS'
'BABS' VALUES IN [(10**-8)*(m**-1)

The data is also provided to the sites in seasonal summary form. It is a summary that is provided in hard copy. The copy is sent to the National Park Service for distribution. The following is a sample of a seasonal summary:

Shenandoah National Park JUN 01,1995 - AUG 31,1995
10/28/97 IMPROVE PARTICULATE NETWORK

Major elements, tracer elements and SO2
24-hour concentrations in nanograms/cubic meter

					Soil elements						Smoke
DATE	HOUR	H	S	SO2	SI	K	CA	TI	MN	FE	KNON
06/03/95	0000	295.0	906.0	330	81.7	40.3	25.2	8.3	*1.4	17.7	29.7
06/07/95	0000	1454.0	4826.0	1626	156.0	58.9	43.3	25.6	*1.9	42.8	33.2
06/10/95	0000	675.0	2468.0	288	121.3	73.2	23.5	*2.9	7.3	30.2	55.1
06/14/95	0000	743.0	1386.0	6307	94.3	58.1	32.8	11.9	*1.8	47.2	29.8
06/17/95	0000	874.0	2311.0	1866	119.0	72.2	33.3	8.9	*1.8	40.8	47.7
06/21/95	0000	720.0	1579.0	570	86.3	63.4	24.1	*2.9	8.2	24.1	48.9
06/24/95	0000	263.0	807.0	171	30.5	17.0	7.6	*2.2	*1.4	3.9	14.6
07/05/95	0000	1223.0	3875.0	269	185.0	63.0	18.7	22.2	*2.2	49.1	33.5
07/08/95	0000	1072.0	2076.0	1745	87.3	107.2	25.3	*2.2	*1.4	19.9	95.3
07/12/95	0000	1641.0	3966.0	1283	94.7	77.2	31.0	*3.2	10.3	31.1	58.5
07/15/95	0000	2208.0	7325.0	3687	304.8	102.0	78.4	30.8	13.2	74.6	57.3
07/19/95	0000	676.0	1976.0	3511	94.1	38.2	32.6	*2.6	*1.7	28.9	20.8
07/22/95	0000	1720.0	5870.0	497	117.5	45.5	25.0	21.4	*2.1	27.2	29.1
07/26/95	0000	825.0	2614.0	356	254.1	43.4	30.5	23.0	3.2	65.6	?4.1
07/29/95	0000	638.0	2090.0	537	307.7	55.2	41.0	19.3	*1.7	78.5	?8.1
08/16/95	0000	2112.0	7686.0	866	322.6	50.1	53.6	55.8	*3.0	105.3	?-13.1
08/19/95	0000	554.0	1041.0	434	96.7	59.0	26.1	8.5	*1.9	31.7	39.9
08/23/95	0000	1081.0	1739.0	3068	99.7	93.1	32.8	*2.7	*1.8	35.9	71.6
08/26/95	0000	377.0	1054.0	1887	71.1	31.0	18.8	9.3	*1.4	23.9	16.7
08/30/95	0000	1023.0	3578.0	1075	127.1	44.8	38.1	29.8	*1.7	59.5	?9.1

		Marine		Metallic tracers							
DATE	HOUR	NA	CL-	V	NI	CU	ZN	AS	SE	BR	PB
06/03/95	0000	*25.30	23.2	*1.97	*0.09	0.42	1.97	0.14	0.42	1.28	0.85
06/07/95	0000	*62.00	14.6	*2.76	*0.10	0.96	7.59	*0.06	2.04	3.21	3.73
06/10/95	0000	*45.80	25.8	11.96	0.72	0.93	4.80	*0.06	0.77	2.35	2.69
06/14/95	0000	65.00	27.0	*2.64	0.47	1.49	13.03	*0.07	1.28	3.78	4.30
06/17/95	0000	*42.90	34.5	*2.66	0.44	1.26	8.85	*0.06	1.52	3.91	3.37
06/21/95	0000	*34.80	26.6	*2.61	*0.10	1.08	5.05	*0.06	0.93	2.71	1.87
06/24/95	0000	57.00	23.5	*2.00	*0.08	0.34	1.16	*0.05	0.32	0.83	1.00
07/05/95	0000	?37.40	18.2	*3.11	0.39	1.15	4.23	*0.07	1.91	2.76	2.60
07/08/95	0000	*35.70	17.5	*2.06	*0.09	1.13	11.25	*0.06	1.79	3.34	2.83
07/12/95	0000	*58.20	34.1	*2.87	*0.10	1.97	11.72	*0.07	2.02	4.32	4.02
07/15/95	0000	*100.80	13.4	*3.87	*0.13	1.74	10.98	*0.08	3.24	4.64	5.13
07/19/95	0000	*37.10	23.7	*2.39	*0.09	1.12	9.49	*0.06	1.25	1.94	3.47
07/22/95	0000	*75.20	14.4	*3.06	0.69	1.29	6.45	*0.07	2.54	2.85	3.39
07/26/95	0000	*43.60	14.4	*2.31	*0.09	1.31	2.84	*0.05	1.06	1.08	1.81
07/29/95	0000	62.60	28.5	*2.52	0.17	0.80	4.06	*0.05	0.86	1.64	1.94
08/16/95	0000	?46.20	?3.6	*4.32	1.53	1.88	13.88	*0.09	2.81	3.86	7.18
08/19/95	0000	142.70	74.7	*2.78	0.79	0.97	3.87	*0.06	0.79	3.54	2.49
08/23/95	0000	42.70	35.3	6.28	*0.10	3.45	10.20	*0.07	1.26	4.04	3.82
08/26/95	0000	121.70	43.8	*2.02	0.39	0.82	4.32	0.36	0.74	2.68	1.83
08/30/95	0000	*50.80	16.5	?5.27	*0.13	1.53	13.92	*0.08	1.55	3.08	5.68

*=minimum detectable limit ?= < (2 x uncertainty) #= MASS>PM10; diff<uncertainty

Shenandoah National Park JUN 01,1995 - AUG 31,1995
10/28/97 IMPROVE PARTICULATE NETWORK
Fine mass and its major components
24-hour concentrations in micrograms/cubic meter

DATE	HOUR	PM10	MASS	RCMC	RCMA	NHSO	NHNO	SOIL	OMCN	OMH	LACN
06/03/95	0000	9.82	7.69	5.48	5.55	3.74	0.40	0.42	1.09	0.94	0.16
06/07/95	0000	31.66	27.97	25.06	25.79	19.91	0.82	0.78	3.76	3.40	0.48
06/10/95	0000	17.29	13.89	13.85	12.82	10.18	0.93	0.52	2.63	?0.79	0.39
06/14/95	0000	20.00	14.89	11.04	13.60	5.72	0.80	0.54	4.08	5.45	0.50
06/17/95	0000	25.38	18.11	15.70	15.94	9.53	0.47	0.57	5.02	4.07	0.45
06/21/95	0000	17.69	13.83	11.77	12.75	6.51	0.43	0.40	4.24	4.47	0.51
06/24/95	0000	8.45	5.29	5.44	4.87	3.33	0.69	0.16	1.44	0.84	0.35
07/05/95	0000	29.21	23.97	21.89	21.39	15.99	0.27	0.86	4.50	3.50	0.41
07/08/95	0000	25.74	20.71	17.36	18.40	8.56	0.54	0.38	7.59	7.60	0.65
07/12/95	0000	33.28	30.76	26.47	27.66	16.36	0.30	0.49	8.86	8.93	0.61
07/15/95	0000	63.10	44.93	39.60	40.13	30.22	0.38	1.40	6.92	5.18	0.86
07/19/95	0000	21.41	14.08	12.13	12.03	8.15	0.57	0.43	3.08	2.50	0.39
07/22/95	0000	38.12	33.45	31.08	30.00	24.21	0.51	0.51	5.74	3.47	0.48
07/26/95	0000	19.06	14.70	14.12	14.92	10.78	0.22	1.21	1.79	2.36	0.28
07/29/95	0000	18.61	13.41	13.22	12.49	8.62	0.51	1.40	2.73	1.59	0.31
08/16/95	0000	42.06		39.19	39.40	31.71	0.41	1.60	4.94	?2.62	0.85
08/19/95	0000	18.63		10.27	10.38	4.29	0.78	0.49	4.72	4.03	0.35
08/23/95	0000	36.85	21.30	17.66	18.82	7.17	0.58	0.52	9.11	8.88	0.66
08/26/95	0000	16.36	8.23	7.23	7.26	4.35	0.40	0.37	1.86	1.56	0.33
08/30/95	0000	26.33	20.16	19.02	19.17	14.76	0.48	0.72	2.88	?1.77	0.58

Fine mass and its major components.
24-hour concentrations in micrograms/cubic meter and percent of fine mass.
BABS in inverse megameters

DATE	HOUR	BABS	MASS	RCMC%	RCMA%	NHSO%	NHNO%	SOIL%	OMCN%	OMH%	LACN%
06/03/95	0000	4.21	7.69	71%	72%	49%	5%	6%	14%	12%	2%
06/07/95	0000	16.66	27.97	90%	92%	71%	3%	3%	13%	12%	2%
06/10/95	0000	12.49	13.89	100%	92%	73%	7%	4%	19%	? 6%	3%
06/14/95	0000	17.46	14.89	74%	91%	38%	5%	4%	27%	37%	3%
06/17/95	0000	17.05	18.11	87%	88%	53%	3%	3%	28%	22%	2%
06/21/95	0000	12.96	13.83	85%	92%	47%	3%	3%	31%	32%	4%
06/24/95	0000	3.94	5.29	103%	92%	63%	13%	3%	27%	16%	7%
07/05/95	0000	9.99	23.97	91%	89%	67%	1%	4%	19%	15%	2%
07/08/95	0000	17.17	20.71	84%	89%	41%	3%	2%	37%	37%	3%
07/12/95	0000	17.82	30.76	86%	90%	53%	1%	2%	29%	29%	2%
07/15/95	0000	32.78	44.93	88%	89%	67%	1%	3%	15%	12%	2%
07/19/95	0000	9.19	14.08	86%	85%	58%	4%	3%	22%	18%	3%
07/22/95	0000	17.19	33.45	93%	90%	72%	2%	2%	17%	10%	1%
07/26/95	0000	6.41	14.70	96%	101%	73%	1%	8%	12%	16%	2%
07/29/95	0000	8.68	13.41	99%	93%	64%	4%	10%	20%	12%	2%
08/16/95	0000	35.51									
08/19/95	0000	12.04									
08/23/95	0000	20.94	21.30	83%	88%	34%	3%	2%	43%	42%	3%
08/26/95	0000	6.96	8.23	88%	88%	53%	5%	4%	23%	19%	4%
08/30/95	0000	19.29	20.16	94%	95%	73%	2%	4%	14%	? 9%	3%

*=minimum detectable limit ?= < (2 x uncertainty) #= MASS>PM10; diff<uncertainty

Shenandoah National Park JUN 01,1995 - AUG 31,1995
10/28/97 IMPROVE PARTICULATE NETWORK

Distribution of Concentrations in nanograms/cubic meter

	Cases	% of cases Significant	Arithmetic Mean	Minimum	Median	Maximum	Maximum occurs
H	20	100%	1008.70	262.99	849.49	2208.34	07/15/95
S	20	100%	2958.61	807.17	2200.27	7686.11	08/16/95
SO2	20	100%	1518.65	171.30	970.70	6306.60	06/14/95
SI	20	100%	142.58	30.45	108.62	322.59	08/16/95
K	20	100%	59.64	16.95	58.53	107.22	07/08/95
CA	20	100%	32.08	7.62	30.73	78.40	07/15/95
TI	20	65%	14.67	2.15	9.11	55.82	08/16/95
MN	20	25%	3.46?	1.37	1.88?	13.16	07/15/95
FE	20	100%	41.90	3.88	33.81	105.32	08/16/95
KNON	20	85%	34.50	-13.08	31.53	95.27	07/08/95
NA	20	30%	59.38?	25.25	48.53?	142.69	08/19/95
CL-	20	95%	25.67	3.60	23.60	74.70	08/19/95
V	20	10%	3.47?	1.97	2.71?	11.96	06/10/95
NI	20	45%	0.33?	0.08	0.13?	1.53	08/16/95
CU	20	100%	1.28	0.34	1.14	3.45	08/23/95
ZN	20	100%	7.48	1.16	7.02	13.92	08/30/95
AS	20	10%	0.08?	0.05	0.07?	0.36	08/26/95
SE	20	100%	1.46	0.32	1.27	3.24	07/15/95
BR	20	100%	2.89	0.83	2.97	4.64	07/15/95
PB	20	100%	3.20	0.85	3.10	7.18	08/16/95

Distribution of Concentrations in micrograms/cubic meter

	Cases	% of cases Significant	Arithmetic Mean	Minimum	Median	Maximum	Maximum occurs
PM10	20	100%	25.95	8.45	23.40	63.10	07/15/95
MASS	18	100%	19.30	5.29	16.50	44.93	07/15/95
RCMC	20	100%	17.88	5.44	14.91	39.60	07/15/95
RCMA	20	100%	18.17	4.87	15.43	40.13	07/15/95
NHSO	20	100%	12.20	3.33	9.08	31.71	08/16/95
NHNO	20	100%	0.52	0.22	0.50	0.93	06/10/95
SOIL	20	100%	0.69	0.16	0.52	1.60	08/16/95
OMCN	20	100%	4.35	1.09	4.16	9.11	08/23/95
OMH	20	85%	3.70	0.79	3.44	8.93	07/12/95
LACN	20	100%	0.48	0.16	0.47	0.86	07/15/95

Distribution of Concentrations in micrograms/cubic meter and percent of fine mass
BABS in inverse megameters

	Cases	% of cases Significant	Arithmetic Mean	Minimum	Median	Maximum	Maximum occurs
BABS	20	100%	14.94	3.94	14.81	35.51	08/16/95
MASS	18	100%	19.30	5.29	16.50	44.93	07/15/95
RCMC%	18	100%	89%	71%	88%	103%	06/24/95
RCMA%	18	100%	90%	72%	90%	101%	07/26/95
NHSO%	18	100%	58%	34%	60%	73%	07/26/95
NHNO%	18	100%	4%	1%	3%	13%	06/24/95
SOIL%	18	100%	4%	2%	3%	10%	07/29/95
OMCN%	18	100%	23%	12%	21%	43%	08/23/95
OMH%	18	88%	20%	6%	16%	42%	08/23/95
LACN%	18	100%	3%	1%	3%	7%	06/24/95

A significant value is greater than 2 times the uncertainty of that value.

?=the percentage of significant values is less than 65%